

Skyrmionics: Materials, Phenomena and Applications

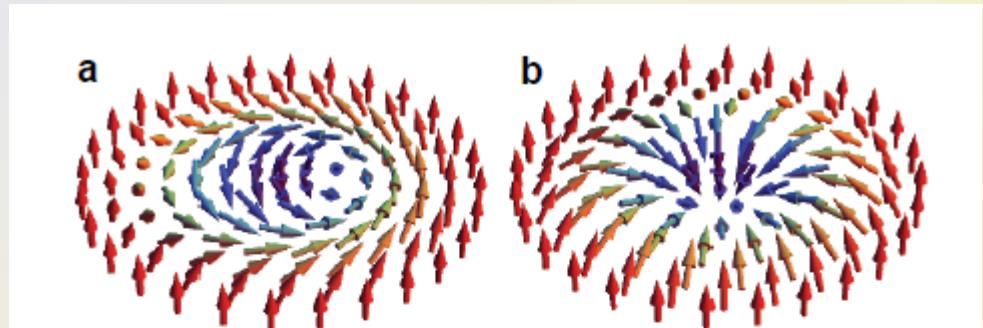
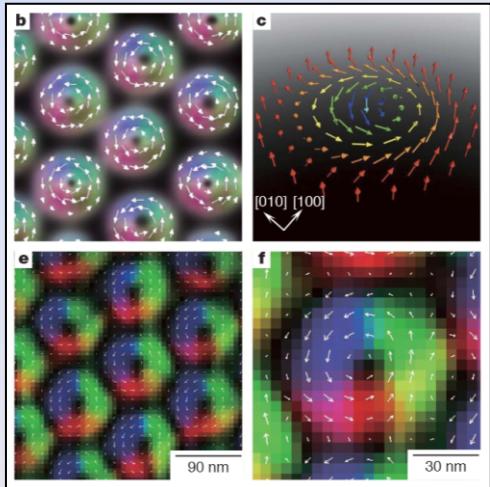
Santa Fe, August 7 - 10, 2017



Skyrmions with ferroelectric polarization

Alois Loidl

Center for Electronic Correlations and Magnetism,
University of Augsburg, 86135 Augsburg, Germany



I. Kézsmárki *et al.*, Nature Mater. **14**, 1116 (2015)

X. Z. Yu *et al.*, Nature **465**, 901 (2010)

FFFFFES

DFG Transregional Research Center TRR 80 (Augsburg, Munich, Stuttgart)
„From Electronic Correlations to Functionality“

Skyrmionics: Materials, Phenomena and Applications

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Skyrmions with ferroelectric polarization

- **Introduction**
Lacunar Spinels: Structure, Jahn-Teller transition, magnetic and ferroelectric phases, orbitally driven ferroelectricity
- **Skyrmion lattices** (easy plane and easy axis anisotropy)
- **Excitations in skyrmion, helical and spin-collinear phases**
- **Summary and Conclusions**

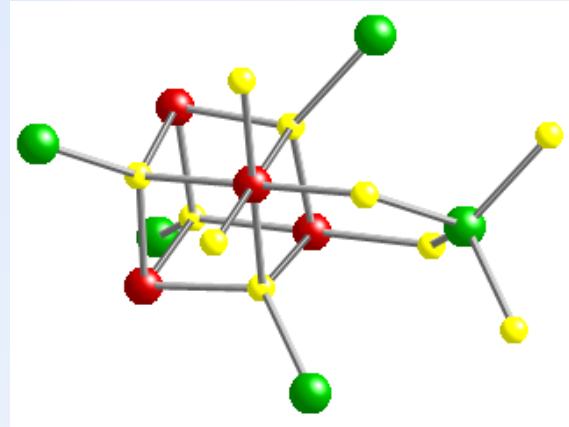
Cooperation and Coworkers:

D. Ehlers, A. Günther, H.-A. Krug von Nidda, P. Lunkenheimer, E. Ruff,
V. Tsurkan, Zhe Wang, S. Widmann
S. Bordacs, I. Kézsmárki (Budapest University of Technology)
I. Stasinopoulos (TU Munich); D. Grundler (EPF Lausanne)

Lacunar spinels AB_4X_8

$A = Ga, Ge$; $B = Cr, Nb, Mo, Ta, Ti, V$; $X = S, Se, Te$

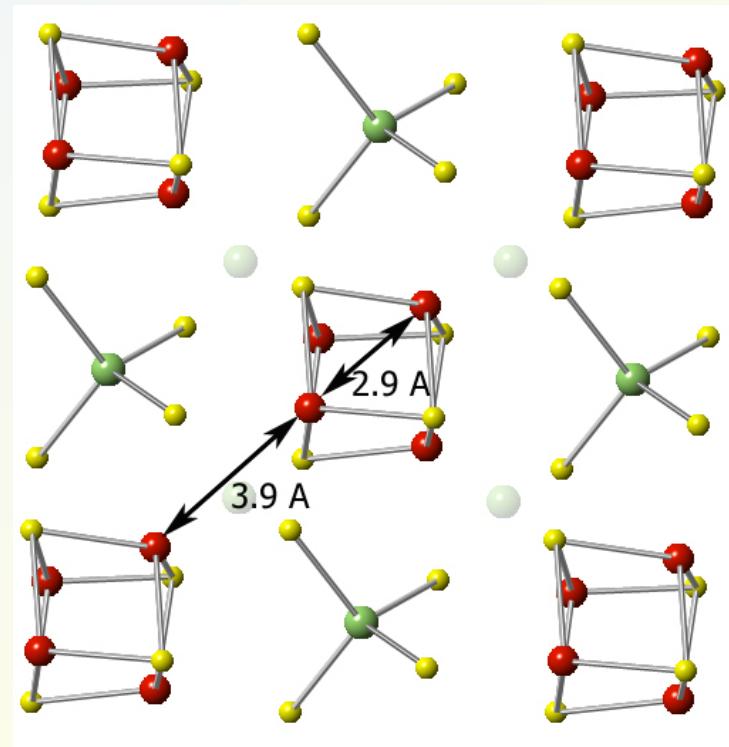
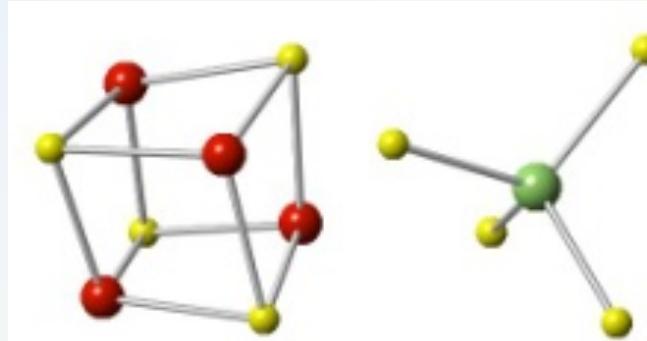
AB_2X_4 spinel, Fd3m (O_h)



Spinel-derived structure

- $\frac{1}{2}$ of **A sites** occupied by non-magnetic A ions
- Frustrated **B sites** occupied by (magnetic/mixed valent) B ions

AB_4X_8 lacunar spinel, F-43m (T_d)



Cubic fcc lattice with cubane like $(V_4S_4)^{n+}$ and tetrahedral $(GaS_4)^{n-}$ molecular units

Lacunar spinels AB_4X_8

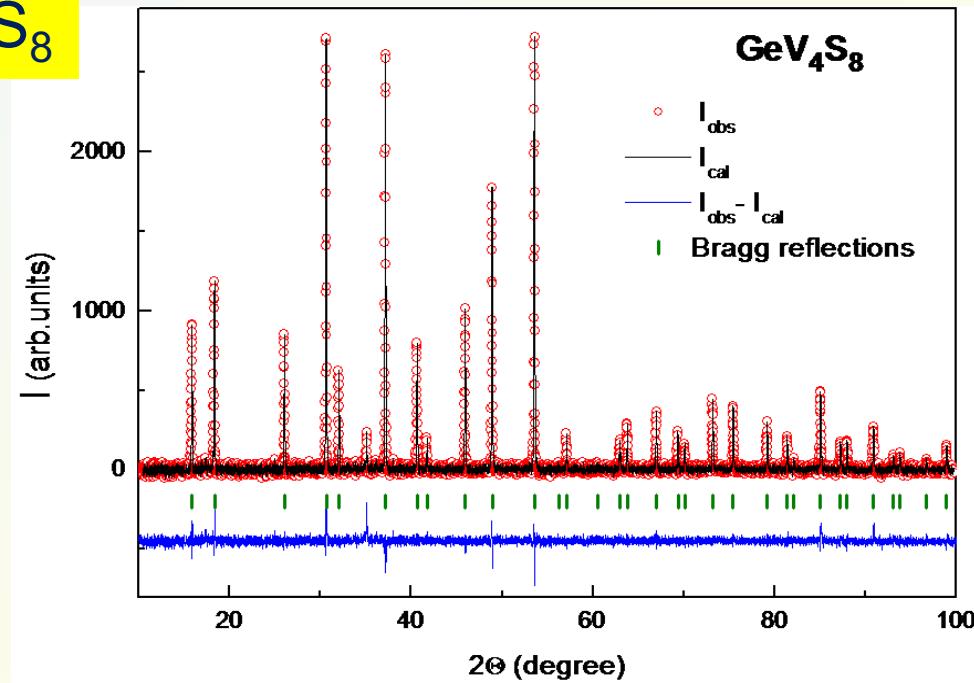
Large group of materials, high-quality single crystals available:

d-derived heavy-fermion behavior, bandwidth-controlled metal-to-insulator transition, large negative magnetoresistance, two-dimensional topological insulating state, electric field-induced resistive switching, pressure induced superconductivity

Orbitally-driven ferroelectricity, multiferroicity, Skyrミon lattice,
Skyrmions with ferroelectric polarization

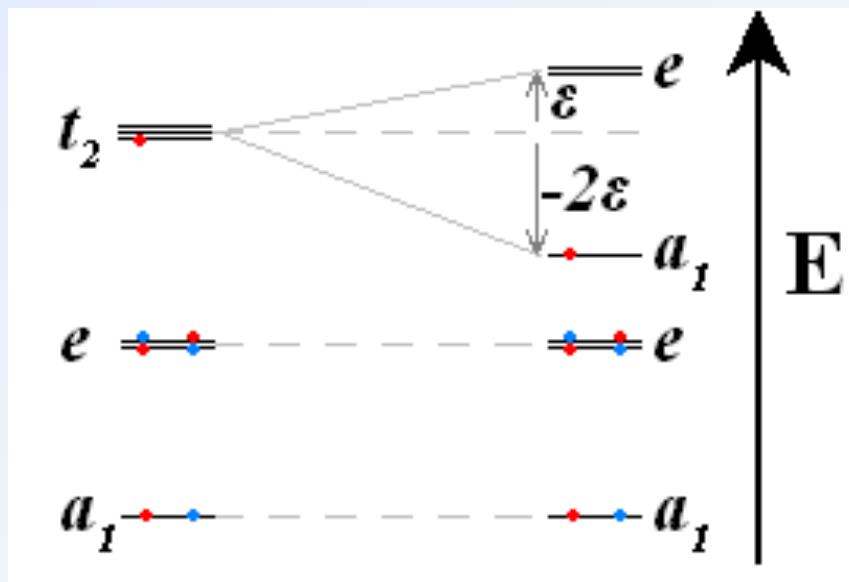
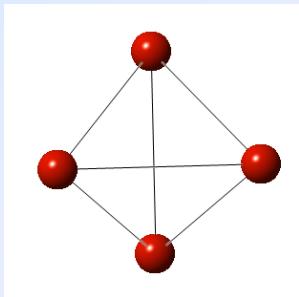


GeV_4S_8

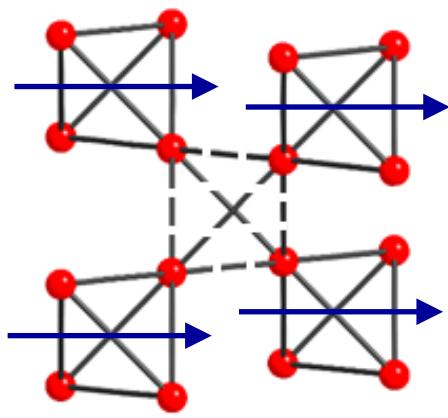
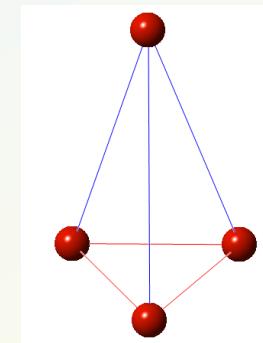


Lacunar spinel GaV_4X_8 : Ga^{3+} , $\text{X} = \text{S}^{2-}$ or Se^{2-} , $\text{V}^{3.25+}$ ($3\text{d}^{1.75}$)

F-43m (T_d)



R3m (C_{3v})



$S=1/2$ per V_4 (3d^7) cluster:

Four tetrahedral V ions constitute magnetic molecule with effective spin $S = 1/2$ (Jahn-Teller active)

In external fields, magnets belonging to crystallographic class C_{3v} can form stable magnetic vortices, analogous to the mixed state of superconductors.

→ Néel-type skyrmions

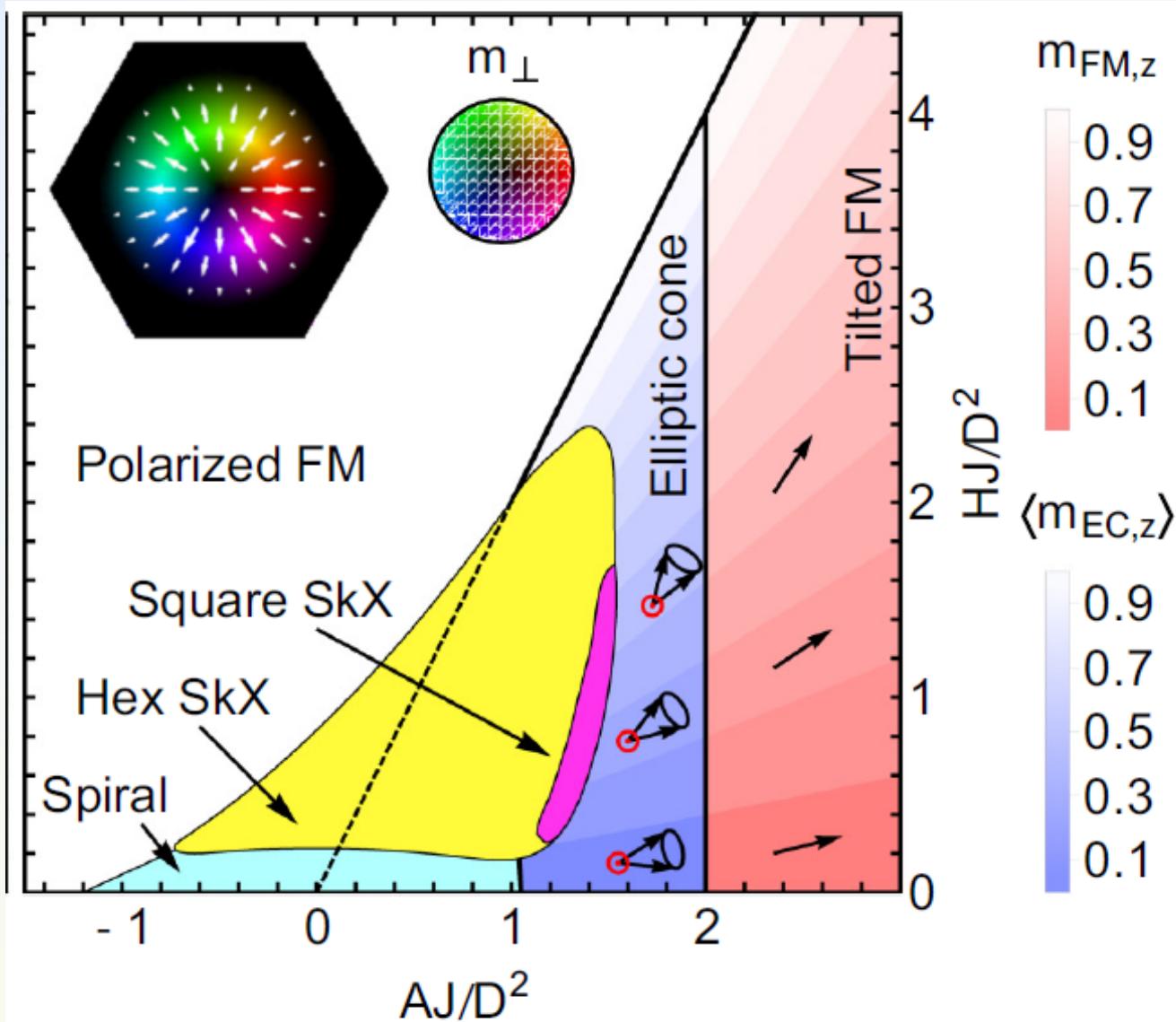
A.N. Bogdanov, D. A. Yablonskii,
Sov. Phys. JETP **68**, 101 (1989)

R. Pocha et al., Chem Mater. **12**, 2882 (2000)

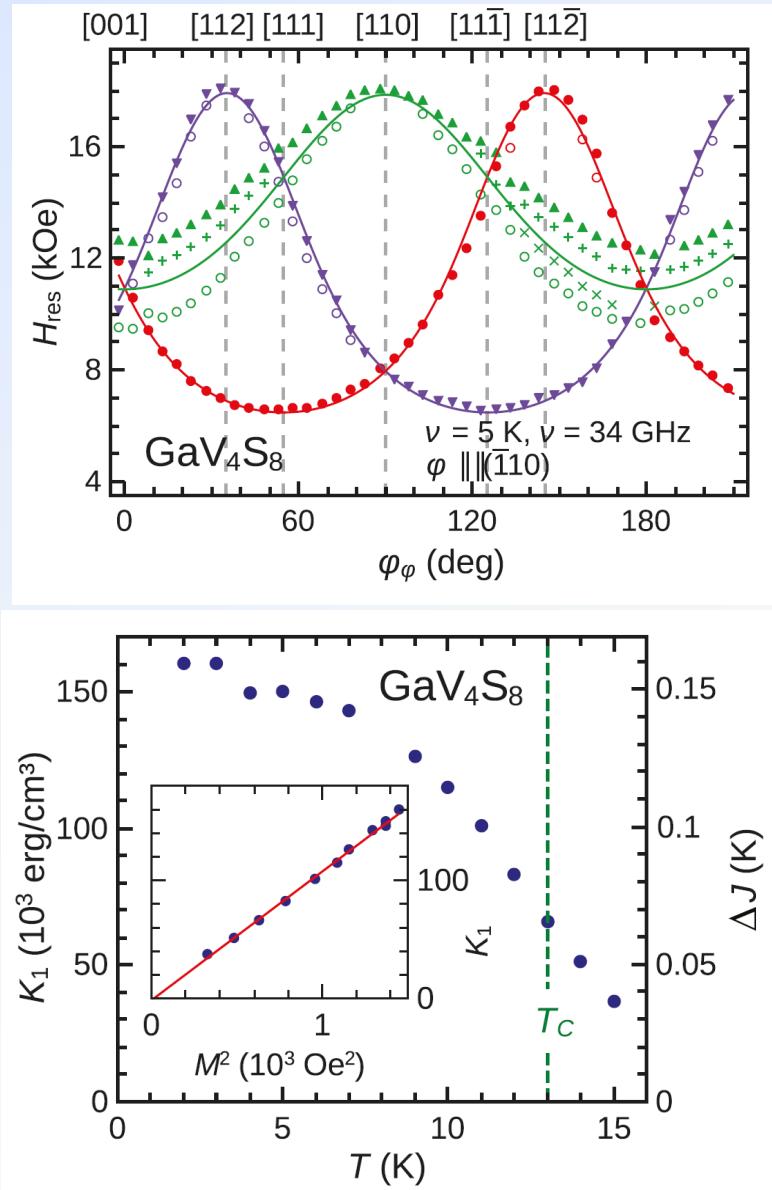
Lacunar spinels: Metals, insulators, multiferroics, and skyrmion hosts with tunable anisotropy

In **easy plane magnets**
with broken mirror
symmetry:

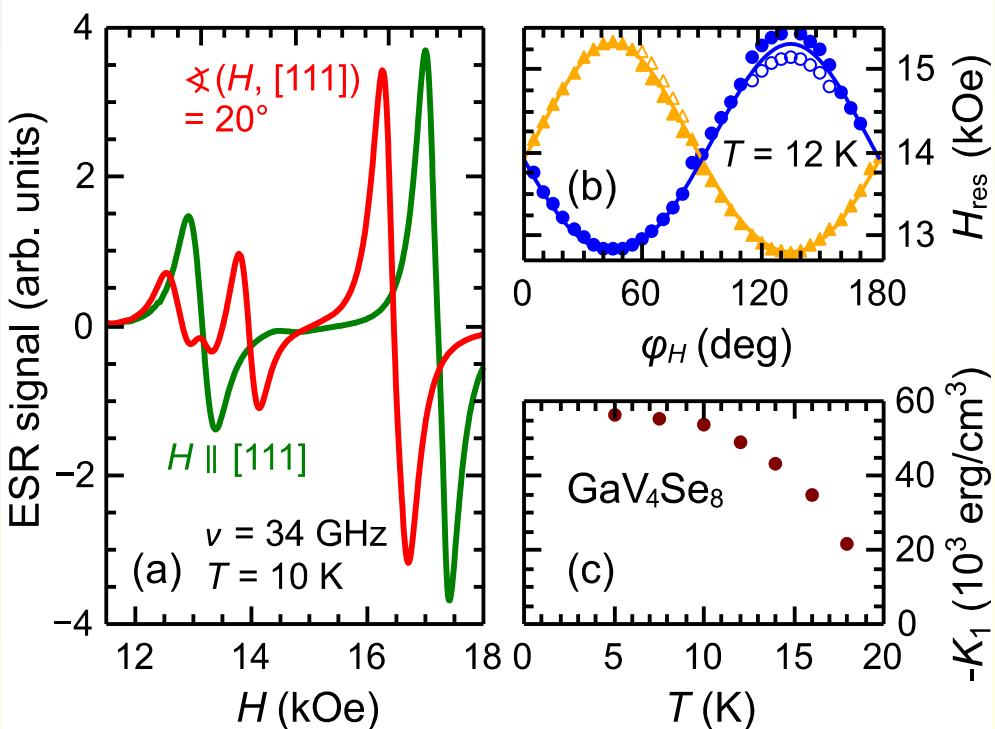
Skyrmion-lattice
significantly extended
+
Square SkX



GaV_4S_8 and GaV_4Se_8 : Magnetic anisotropy

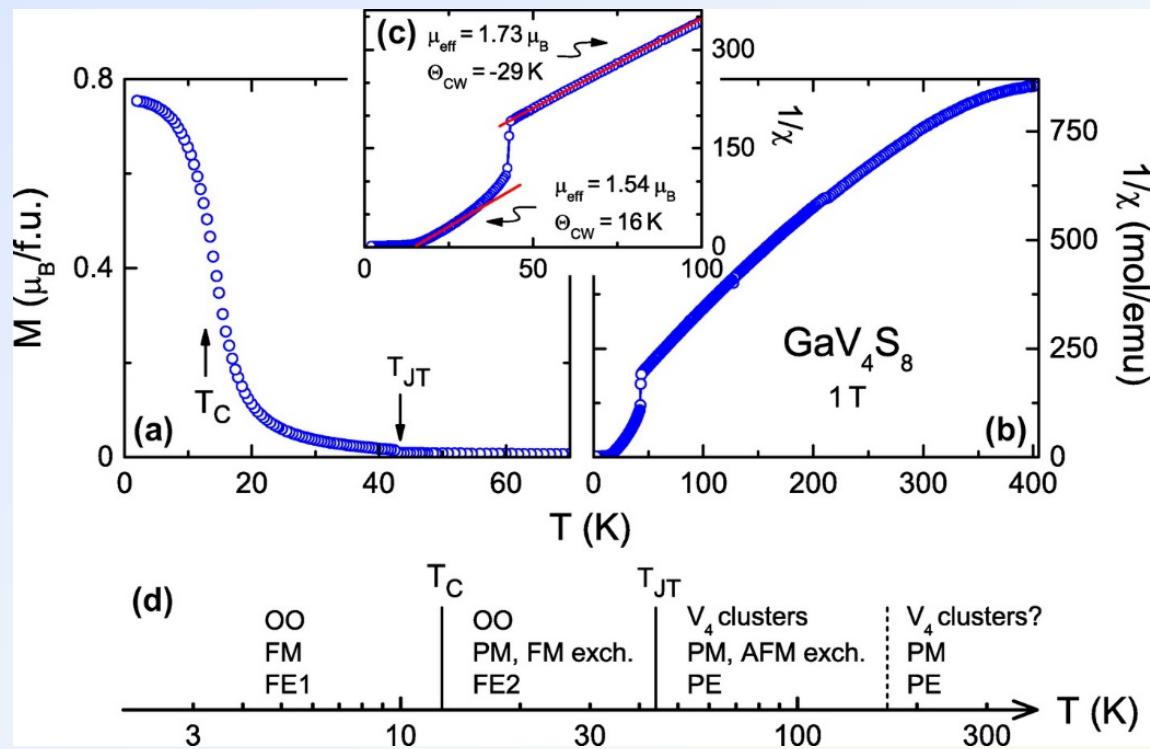


X- and Q-band ESR:
Magnetic resonance in FM state
 GaV_4S_8 : strong easy-axis ferromagnet
 GaV_4Se_8 : weak easy plane ferromagnet



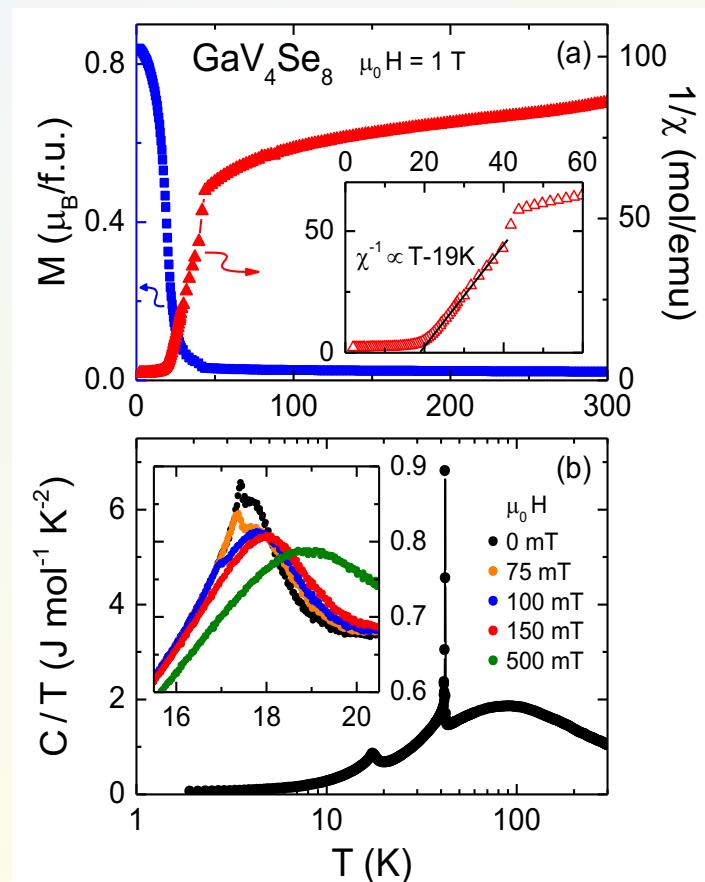
S. Bordács et al., Sci. Reports 7, 7584 (2017)

GaV_4S_8 and GaV_4Se_8 : Magnetic properties



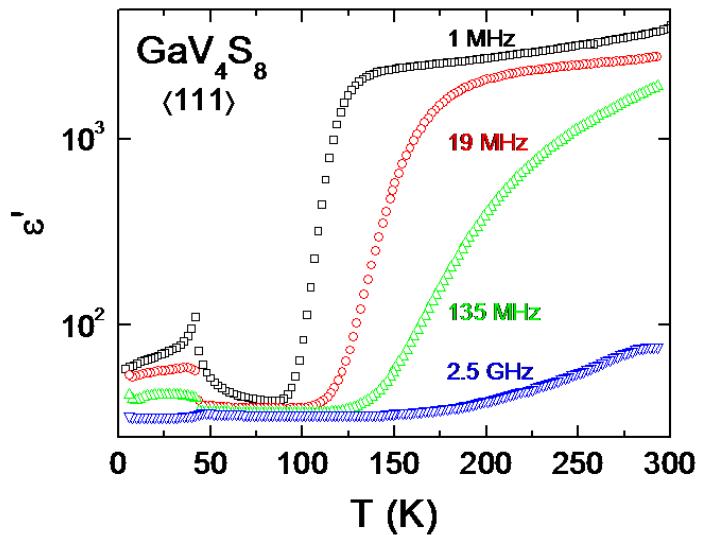
S. Widmann et al., Phil. Magazine (2016), DOI: 10.1080/14786435

In external magnetic fields of 1T
spontaneous magnetization
with ordered moment close to $S = \frac{1}{2}$ system.

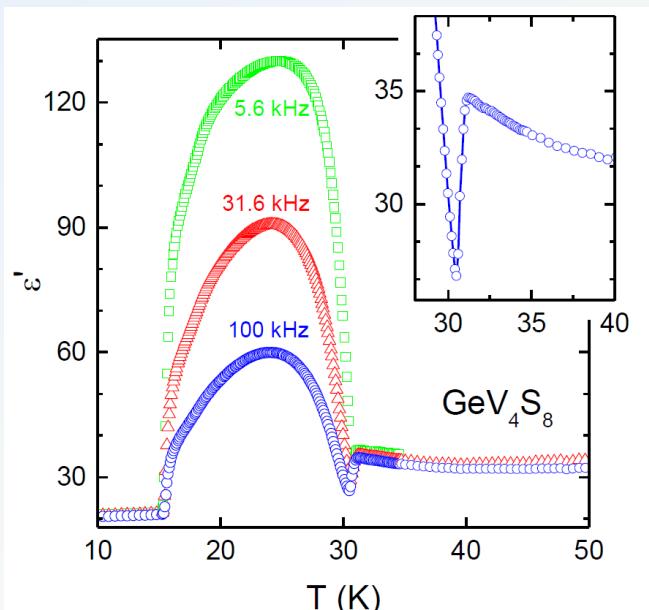


V. Tsurkan, S. Widmann et al., (2017).
unpublished

Lacunar spinels: Jahn-Teller driven ferroelectricity

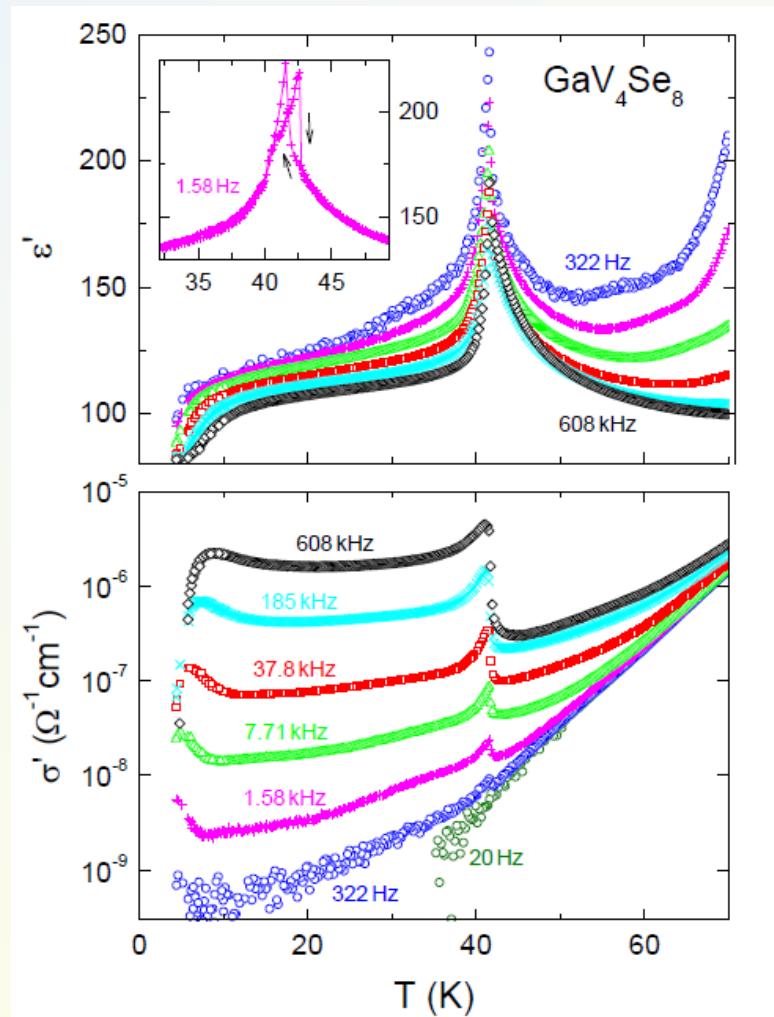


E. Ruff *et al.*, Science Advances **1**, e1500916 (2015)



S. Widmann *et al.*, Phys. Rev. B **94**, 214421 (2016)

Dielectric spectroscopy on lacunar spinels:
Ferroelectric phase transition at
onset of orbital order



E. Ruff *et al.*, unpublished, (2017)

GaV_4S_8

Sample characterization

GaV_4Se_8

Jahn-Teller transition at

$$T_{JT} = 44 \text{ K}$$

$$T_{JT} = 42 \text{ K}$$

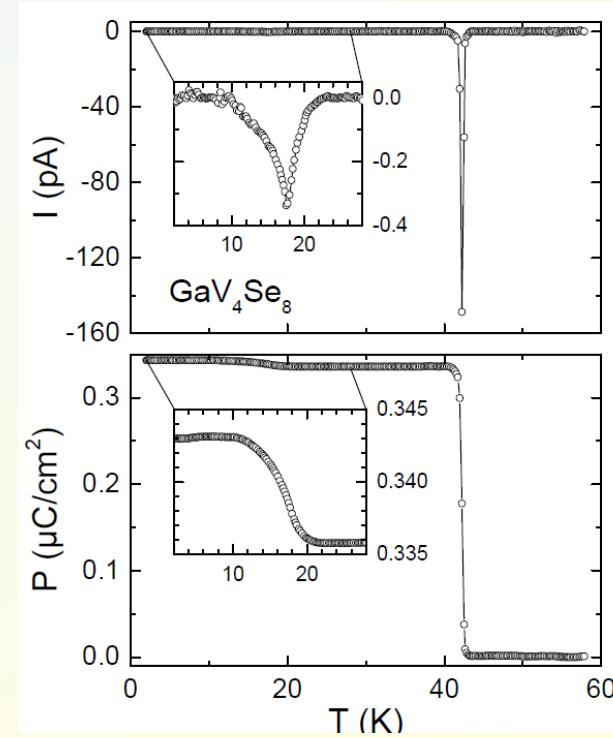
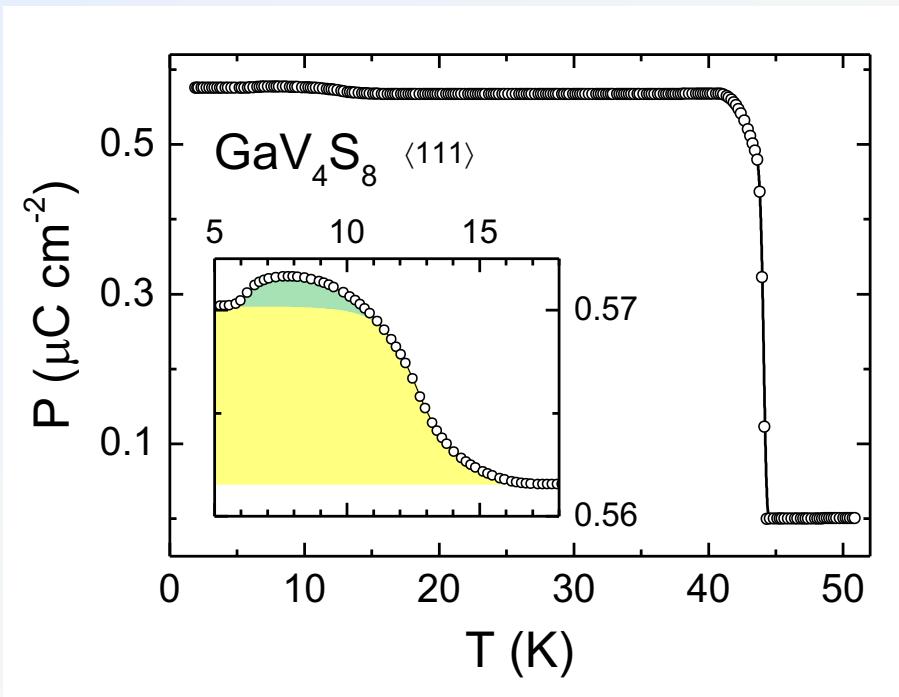
induces ferroelectricity

Complex magnetic order below

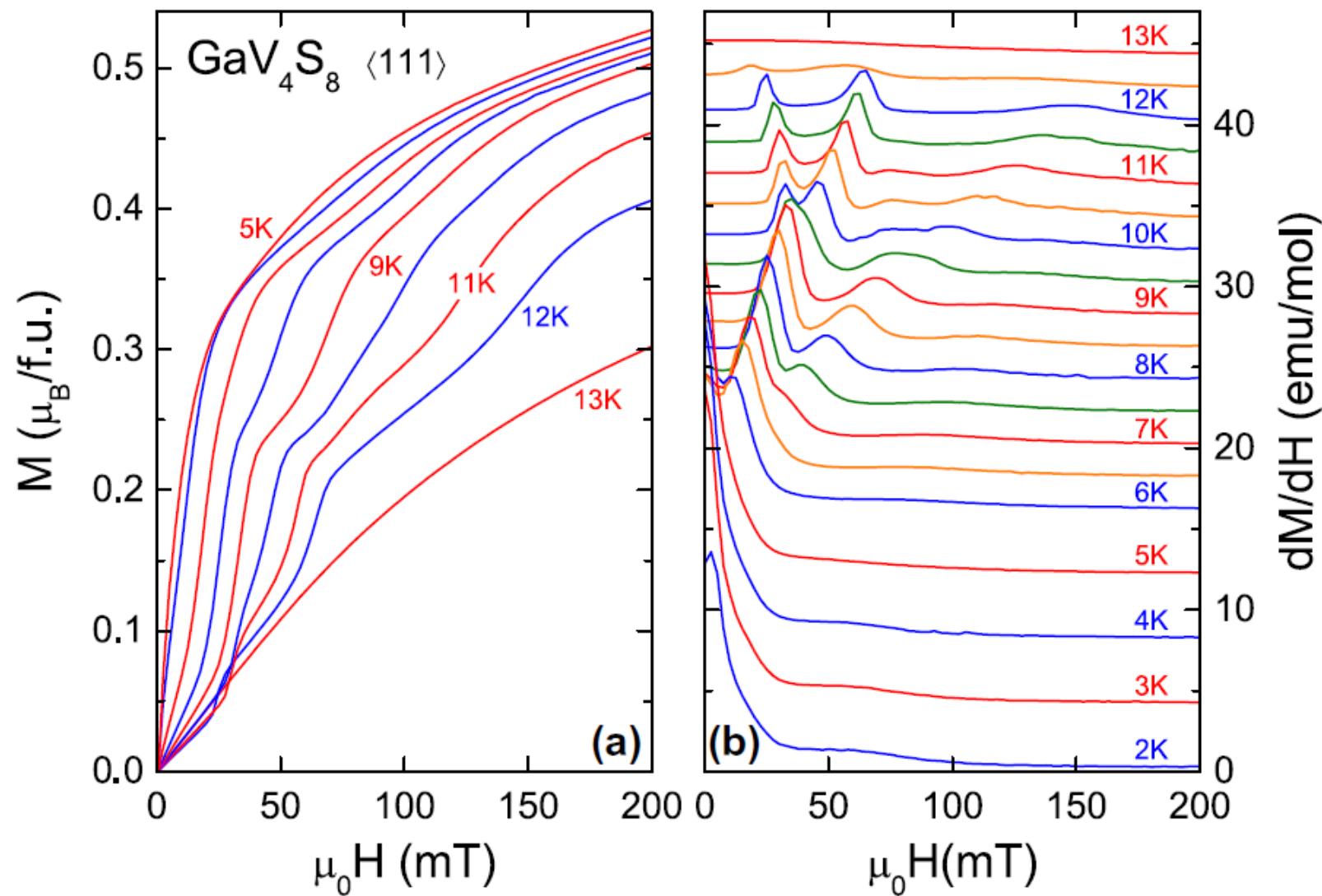
$$T_c = 12.7 \text{ K}$$

$$T_c = 17.5 \text{ K}$$

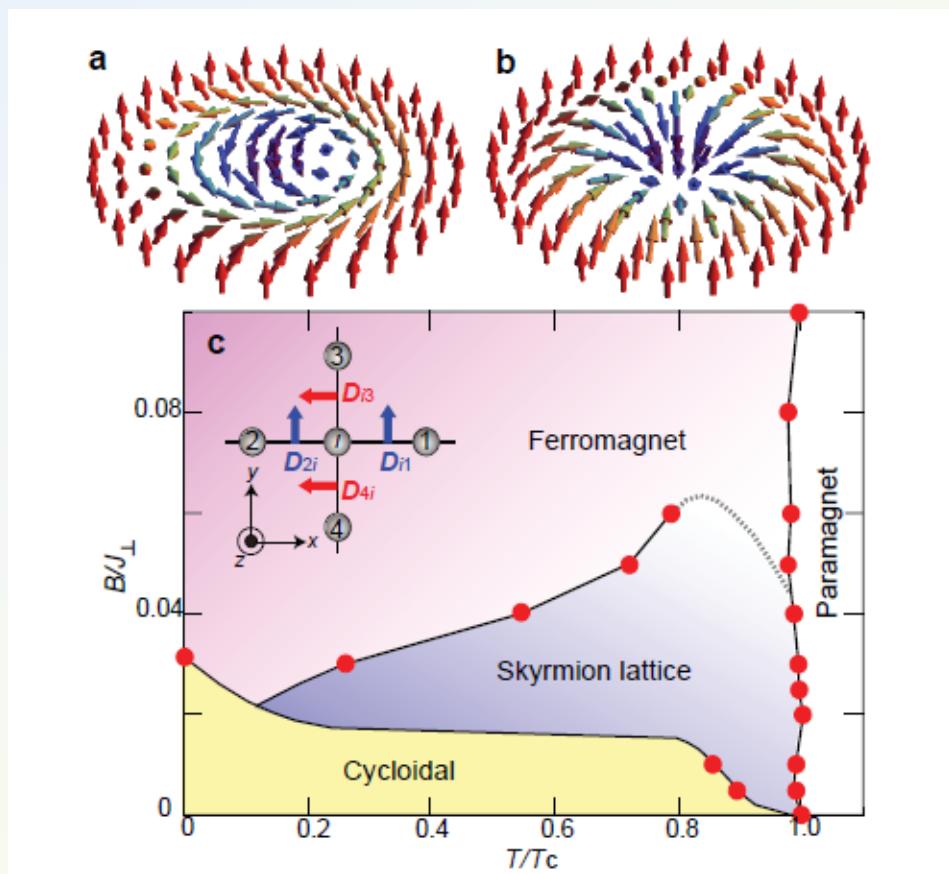
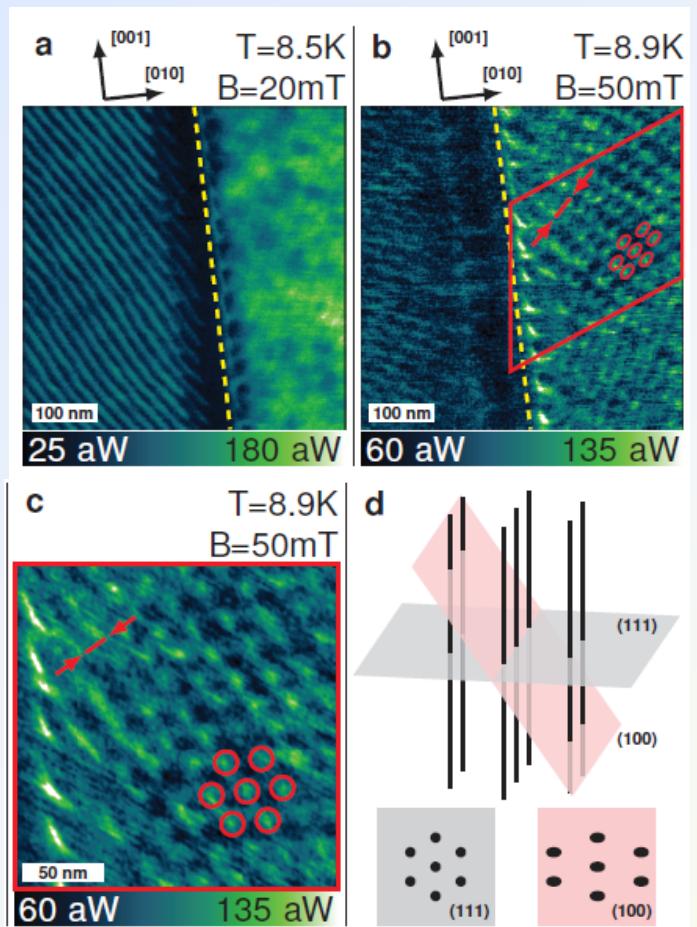
induces additional spin-driven polarization



GaV_4S_8 : Magnetization and susceptibility



GaV_4S_8 : Skyrmiон lattice



Real-space imaging of magnetic patterns:

AFM image at $T=8.5/ 8.5$ K and in $B=20/ 50$ mT on (100) surface .

Color coding corresponds to dissipated power due to magnetic interactions between tip and sample.

Néel-type skyrmions (b) in GaV_4S_8 contrasted to Bloch-type skyrmions (a). (Theoretical phase diagram of GaV_4S_8 by M. Mochizuki)

GaV_4S_8 : Magnetic phases

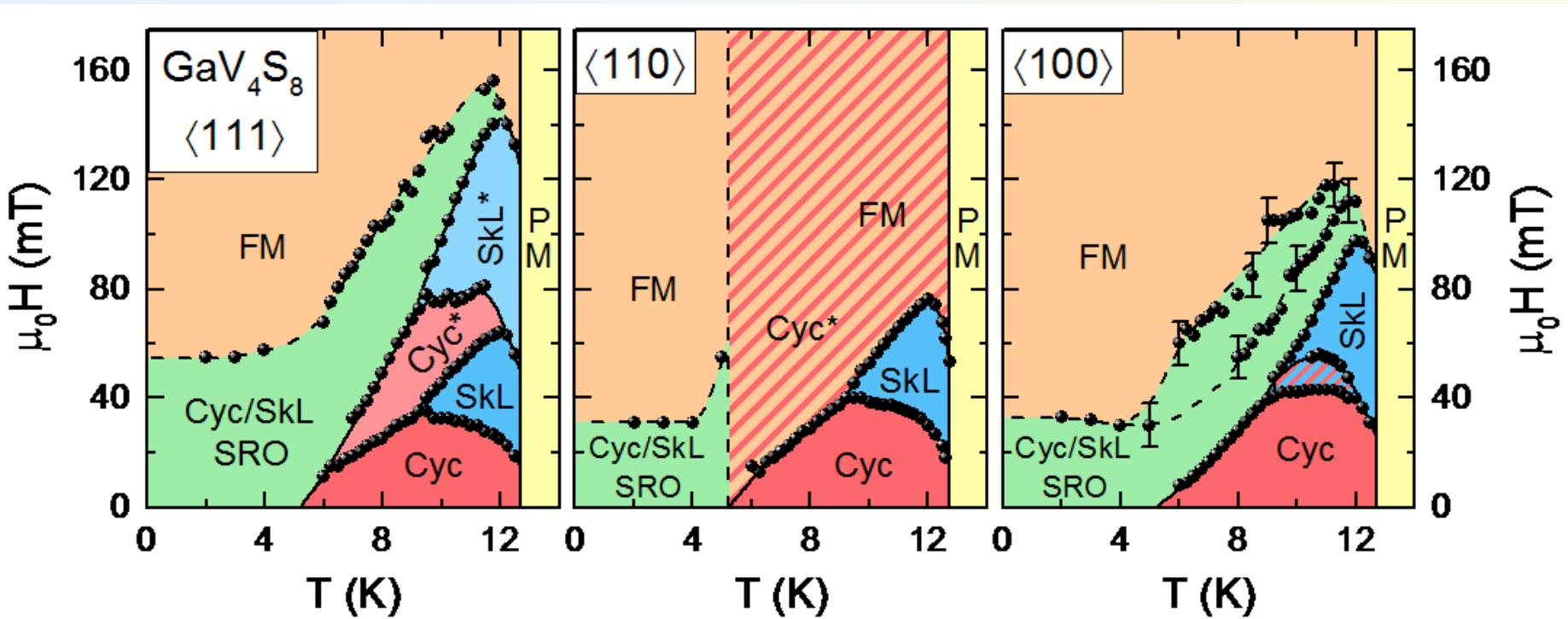
Magnetic phase diagram much more complicated as previously anticipated:

Low temperatures and low fields: Purely ferromagnetic/collinear (FM) spin order?

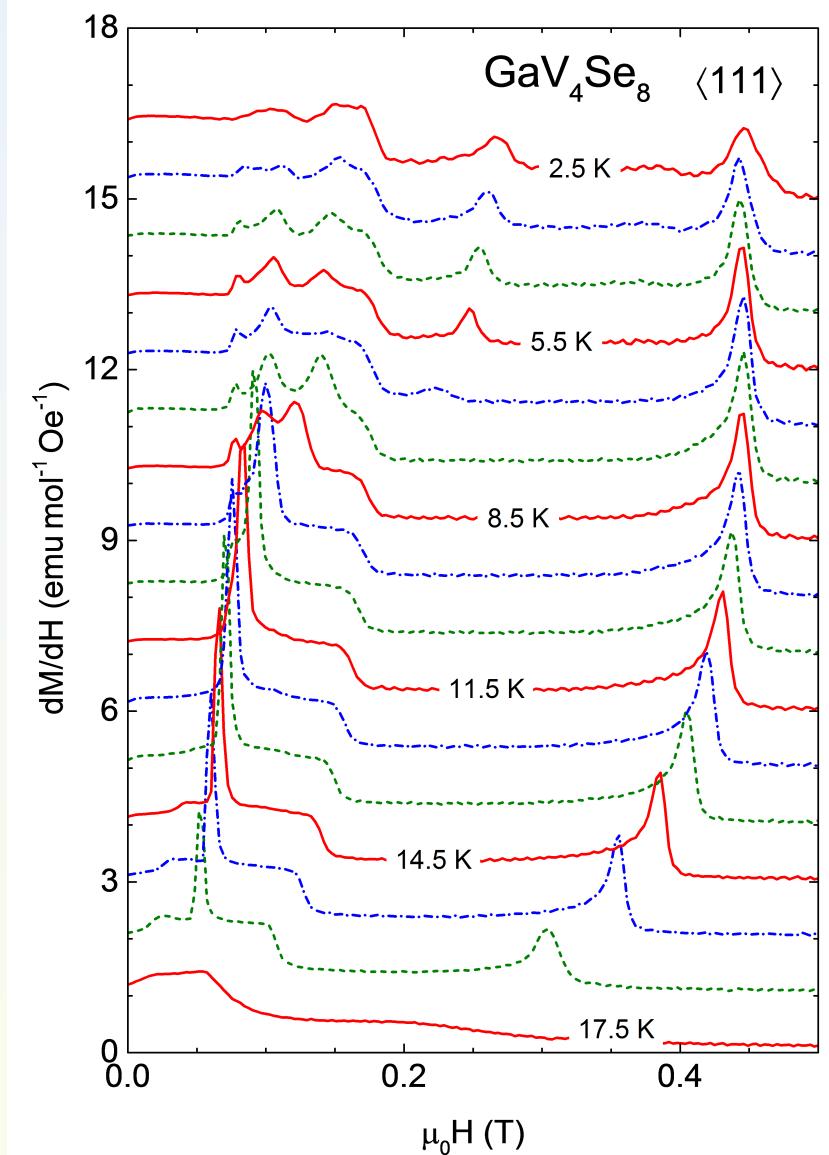
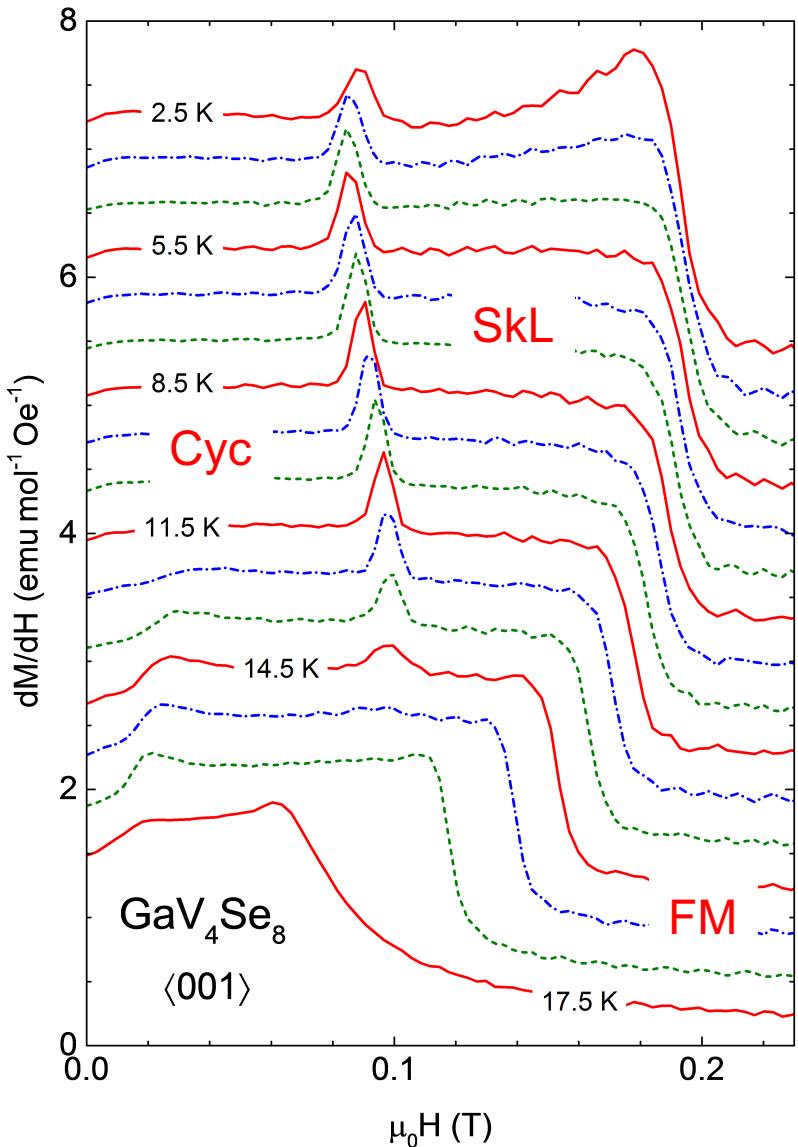
Short-range order (SRO) phases of cycloidal (cyc) and skyrmion lattice (SkL) exist

Metastable states with long relaxation times (**glassy phenomena?**)

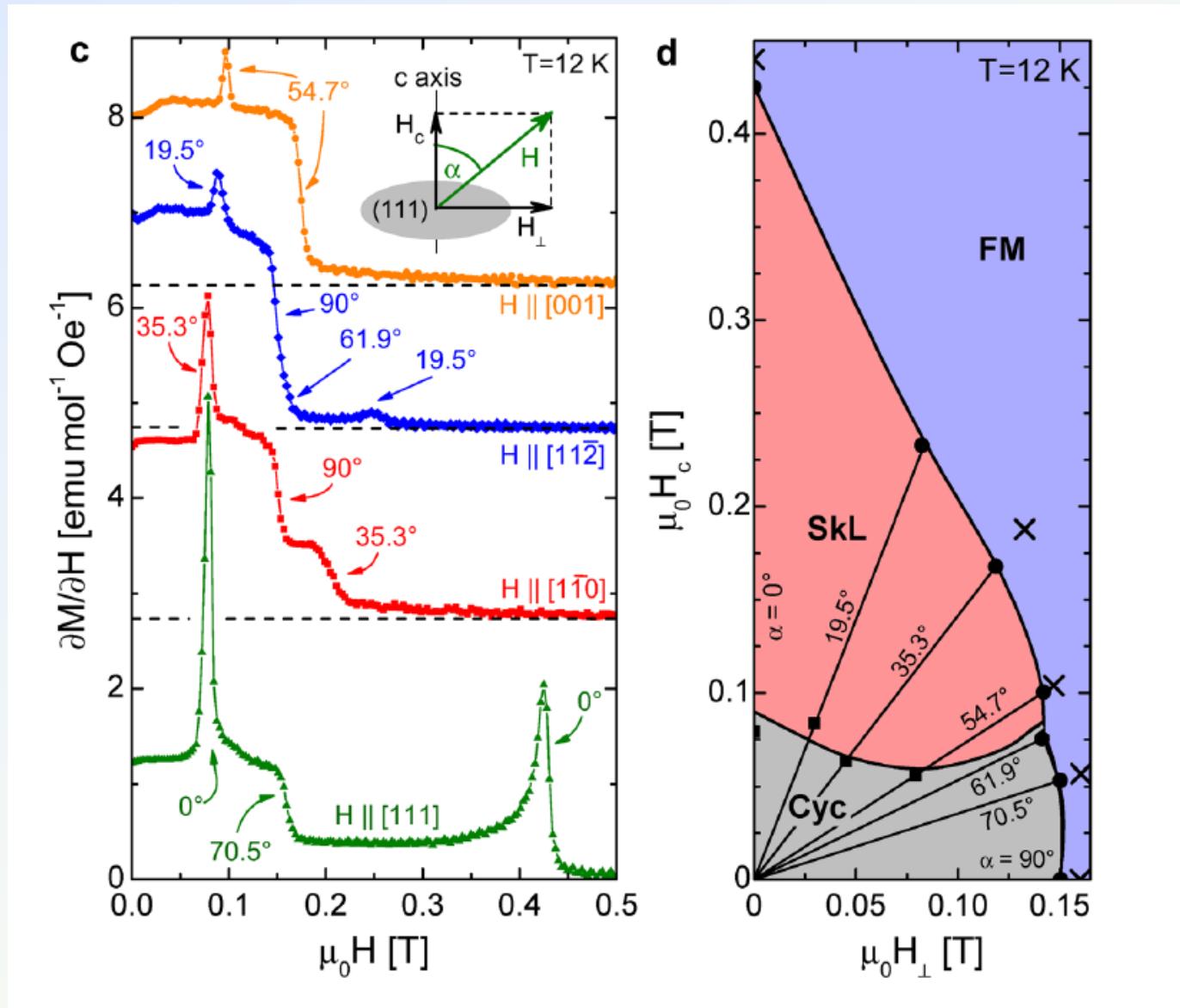
A. Butykai et al., arXiv: 1703.10928



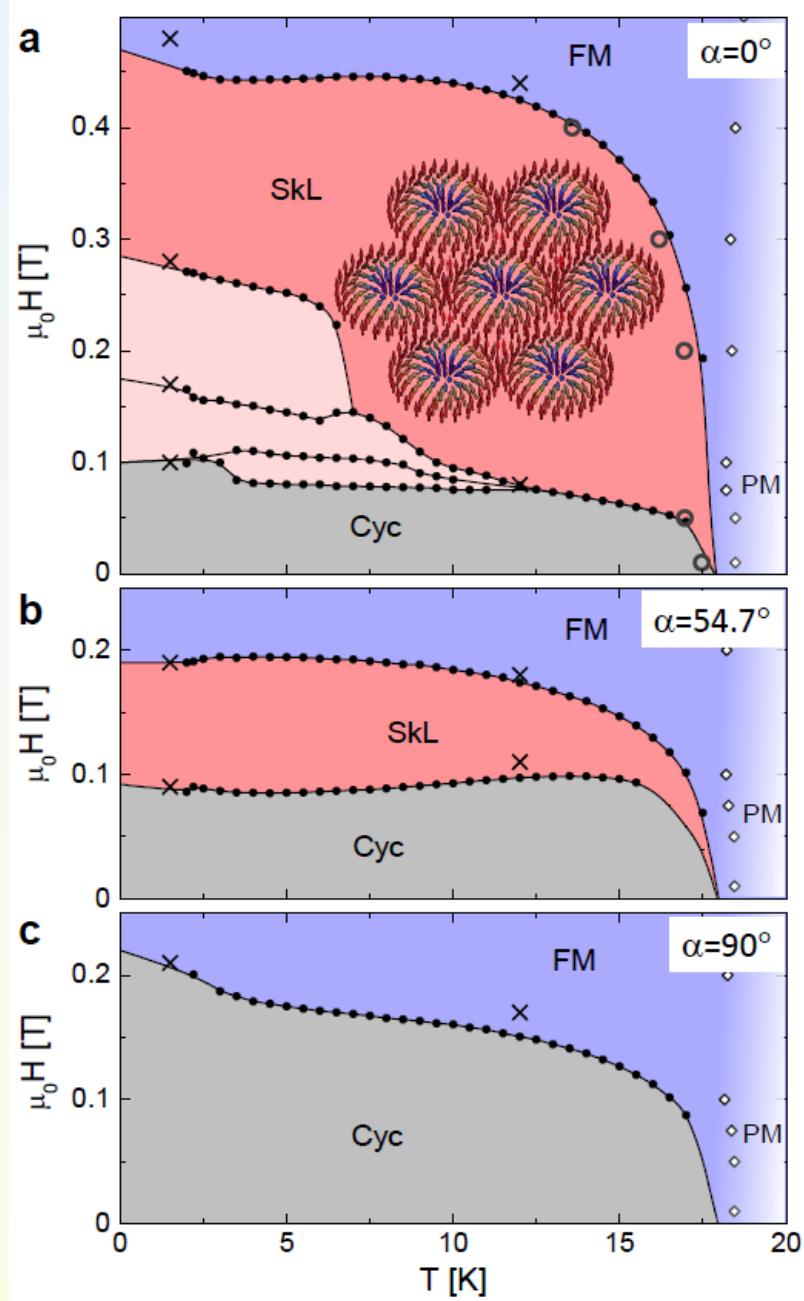
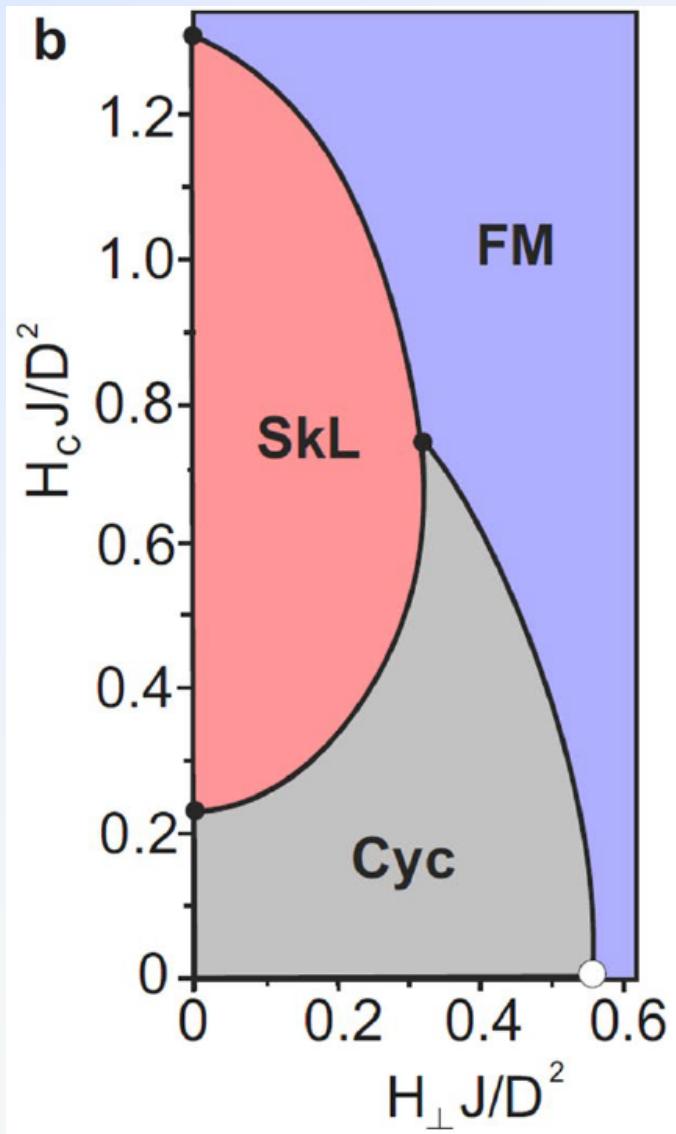
GaV_4Se_8 : Magnetic phases



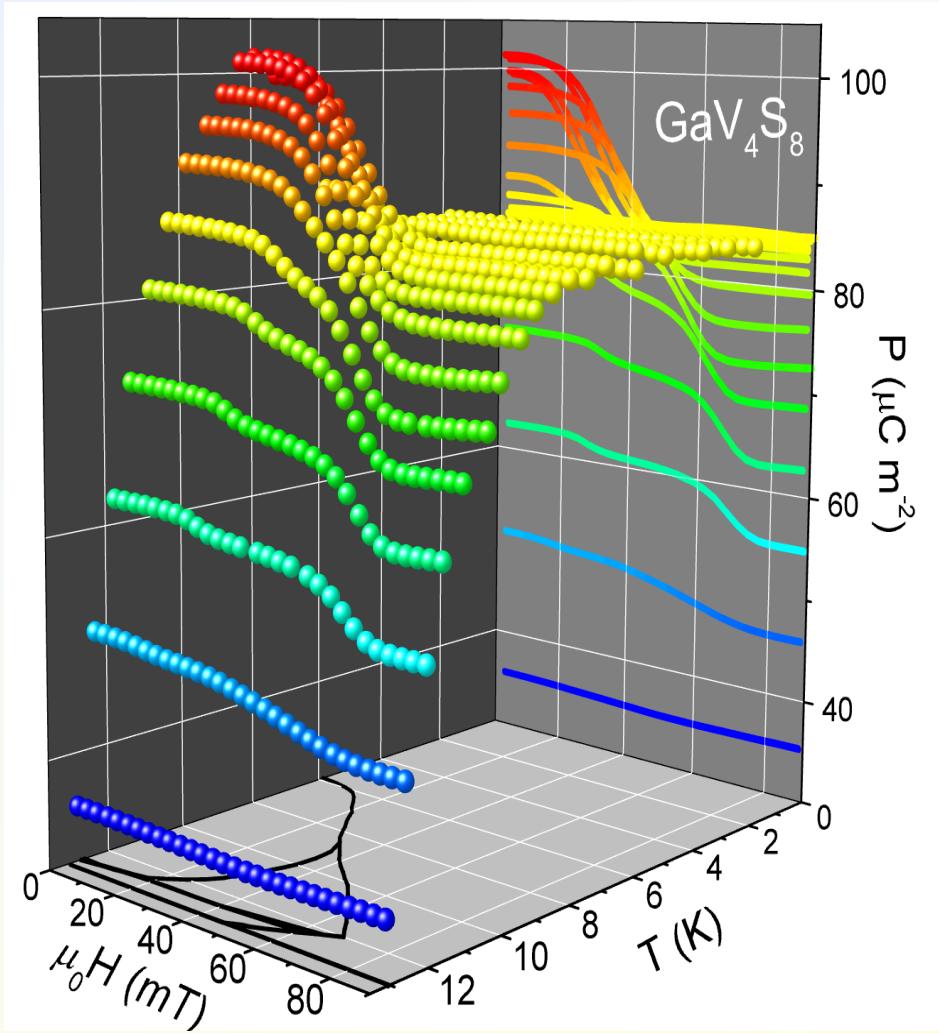
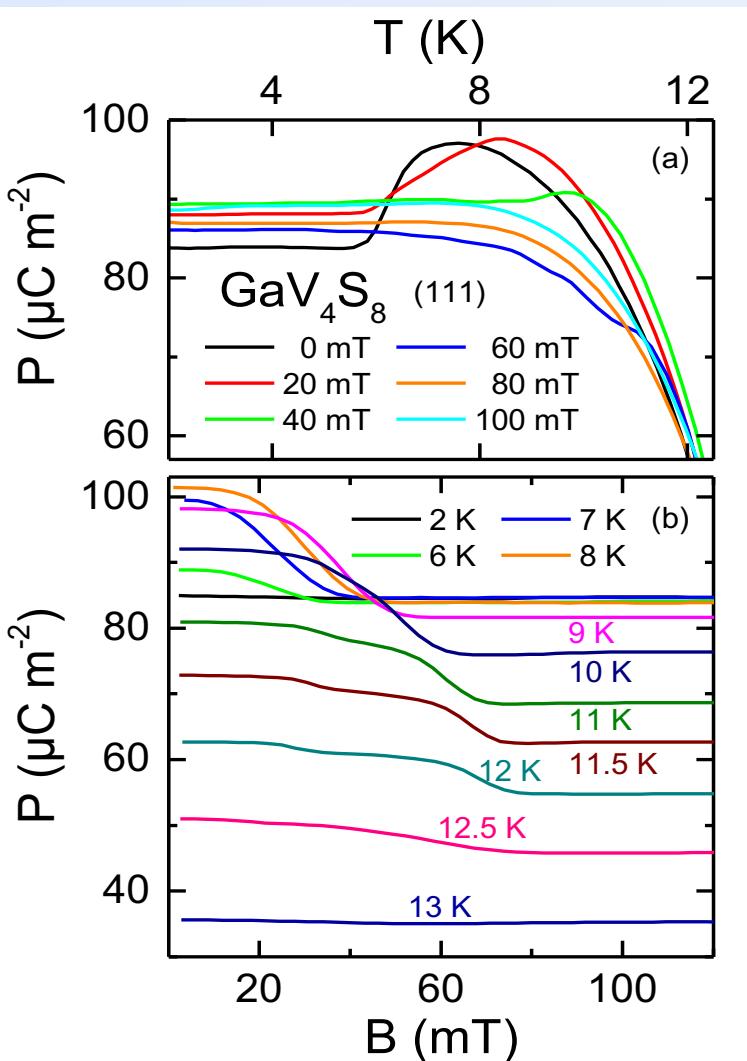
GaV₄Se₈: Magnetic phase diagram



GaV_4Se_8 : Magnetic phase diagram

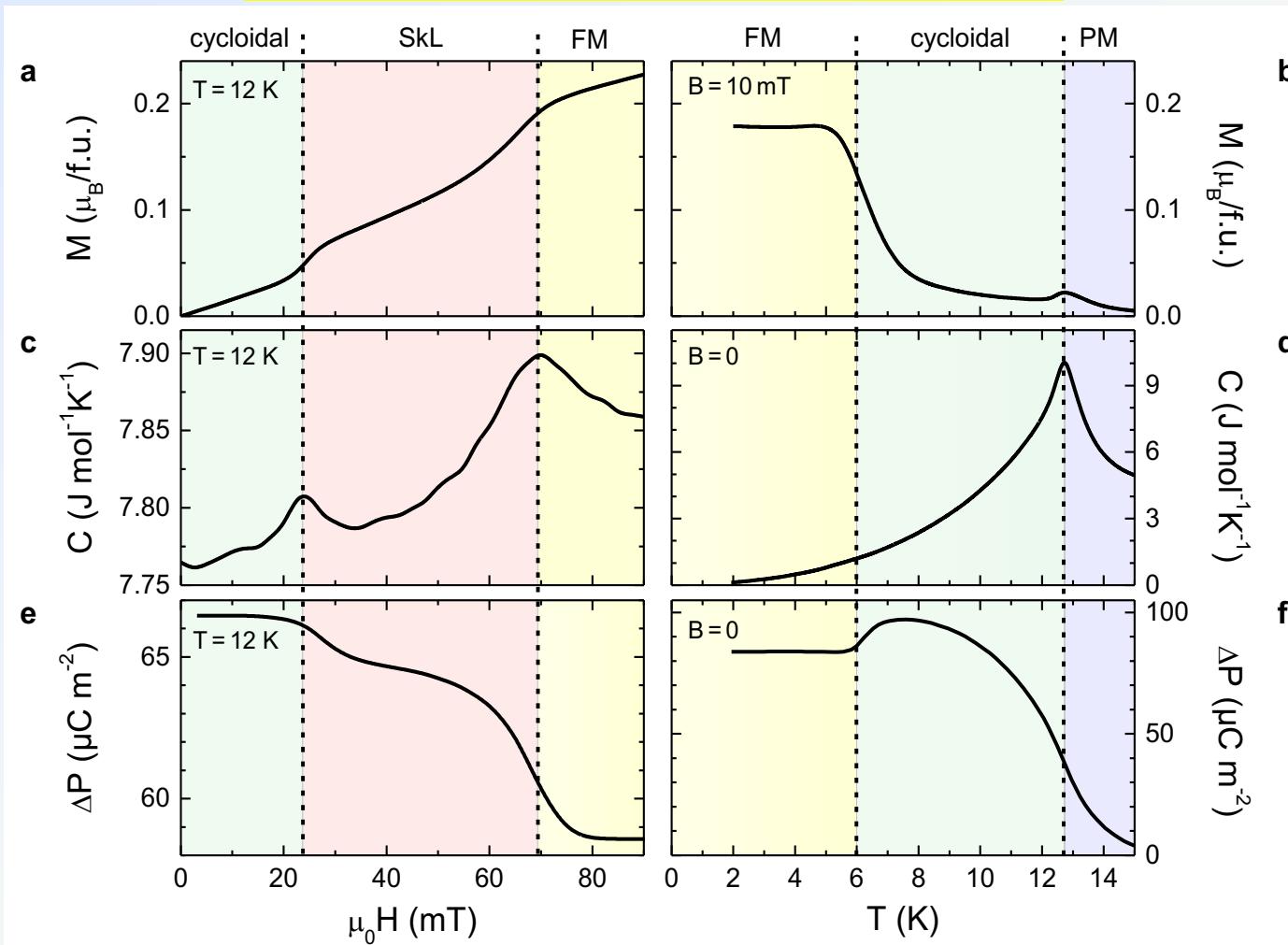


GaV_4S_8 : Multiferroicity



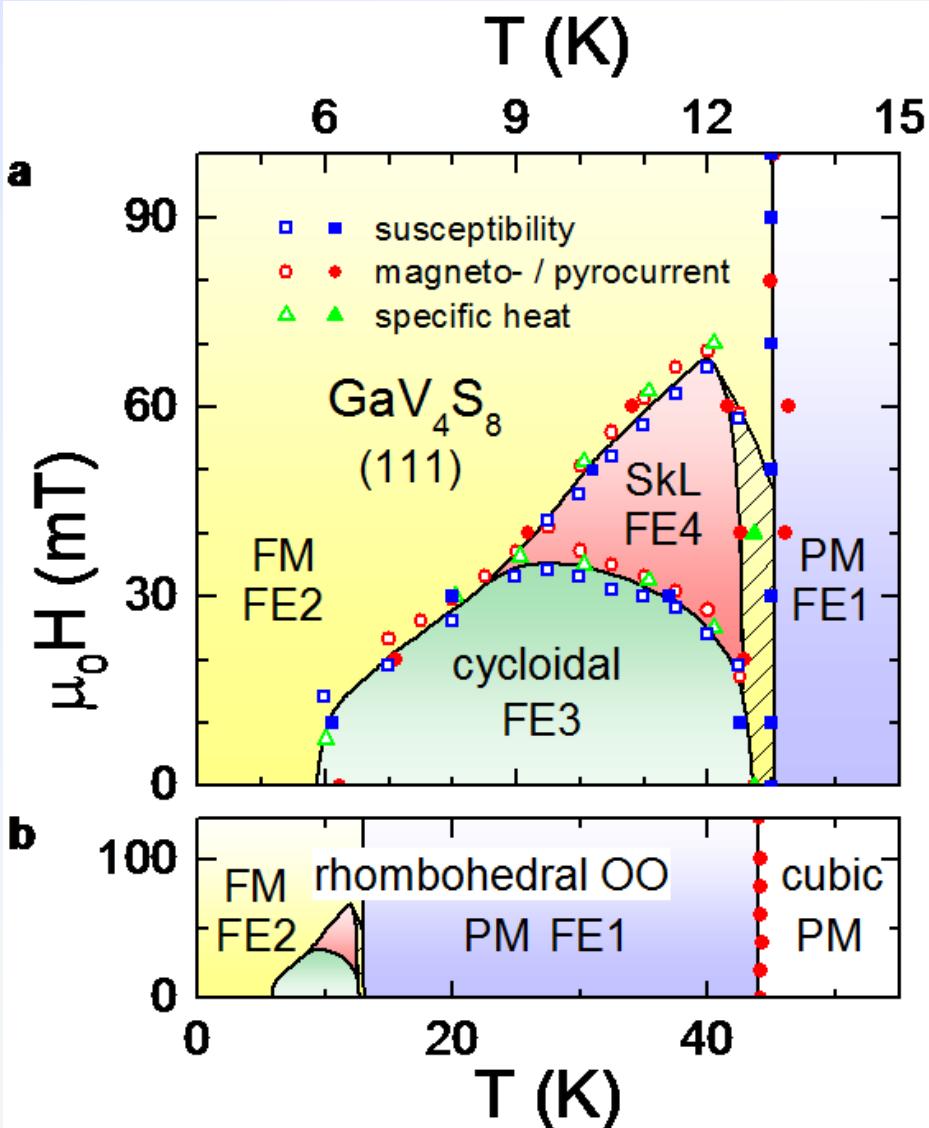
Ferroelectric polarization of GaV_4S_8 from magnetocurrent and pyrocurrent measurements:
Magnetic field dependence of isothermal polarization between 2 and 13 K.

GaV₄S₈: Multiferroicity



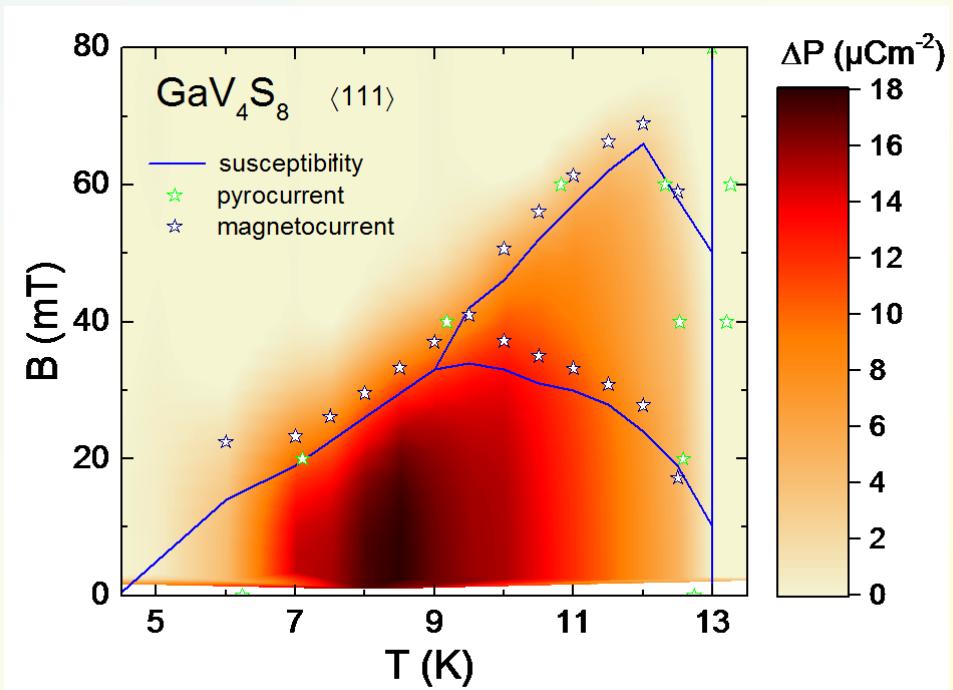
Anomalies in the ferroelectric polarization, specific heat and magnetization at magnetic phase boundaries: (a)-(c) Magnetic field dependence of isothermal polarization (ΔP), specific heat (C) and magnetization (M). (d)-(f) Temperature dependence of zero-field polarization, specific heat and magnetization

GaV_4S_8 : Magnetic and polar phases



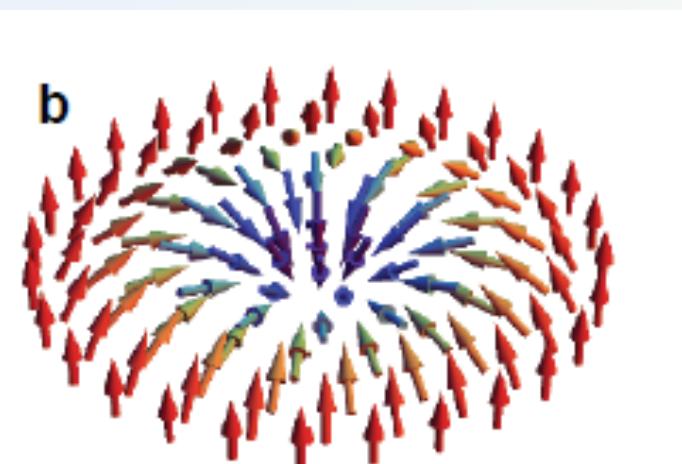
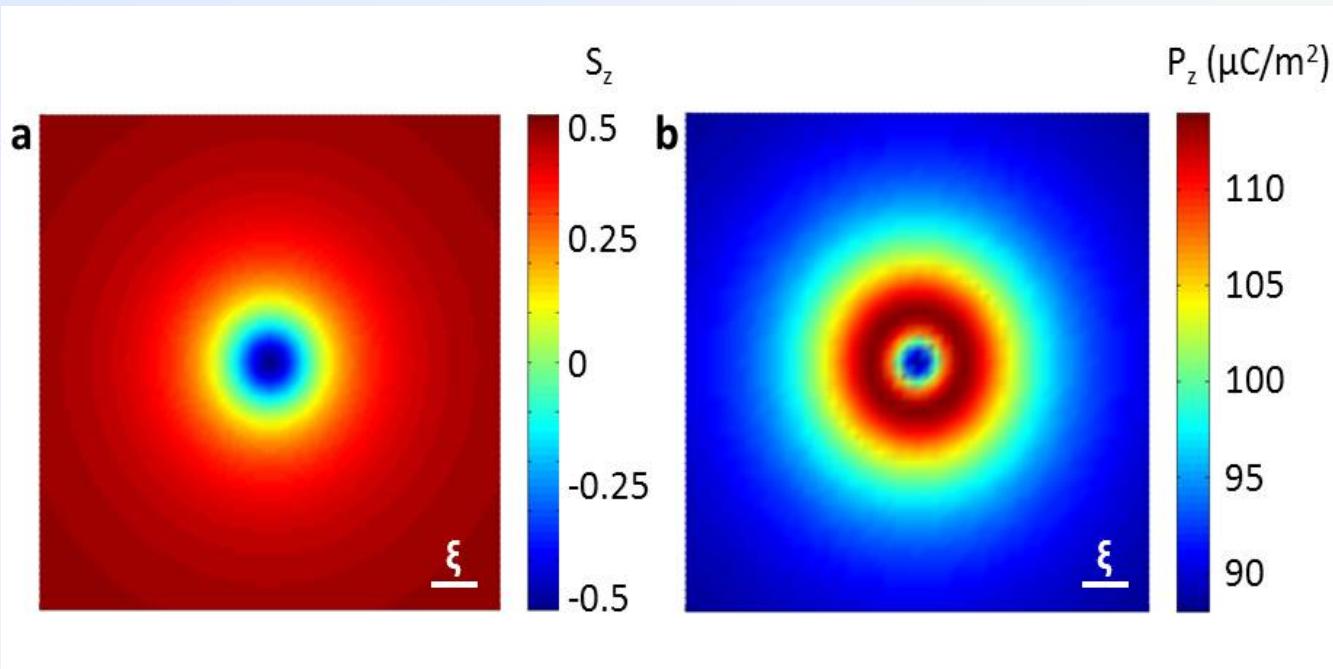
(H,T)- phase diagram of GaV_4S_8 for magnetic fields along $\langle 111 \rangle$:

- Low-temperature region at $T < 15$ K and
- complete phase diagram extending beyond Jahn-Teller transition.



Excess polarization ΔP in (H,T) - plane

GaV_4S_8 : Polar skyrmions



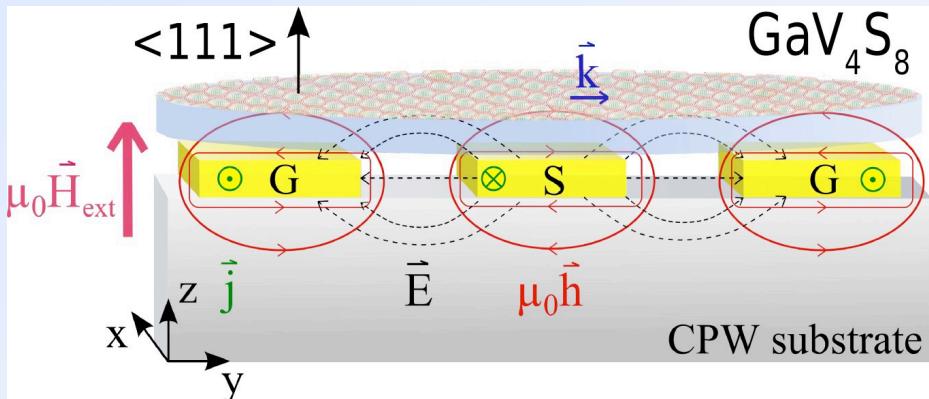
Polar dressing of the SkL in GaV_4S_8

- (a) Spatial dependence of z component of $S = 1/2$ spins forming skyrmion
- (b) spatial dependence of spin-driven polarization \mathbf{P}_z (in plane perpendicular to vortex core).

Radius of skyrmion core ξ sets lateral length scale. Polarization reaches maximum in ring-like (red) region around skyrmion cores. Outer blue regions indicate FE polarization of almost collinear spin arrangement at outer rims of skyrmion.

GaV_4S_8 : CPW absorption spectroscopy

In cooperation with
D. Grundler, EPFL (CH)



Pioneering work:

Cu_2OSeO_3 :

Y. Okamura, Nat. Commun. **4**, 2391 (2013)

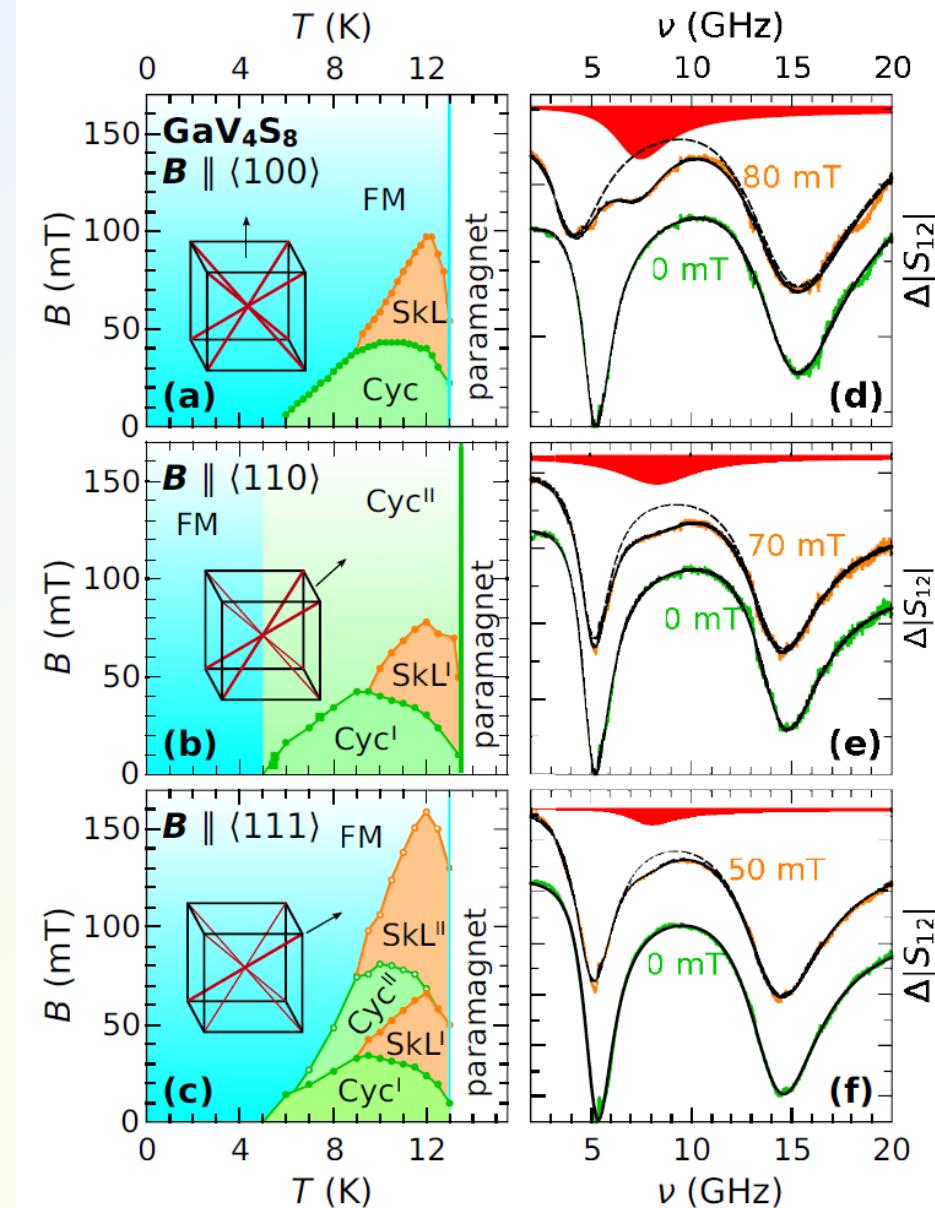
B20 compounds:

T. Schwarze et al., Nat. Mater. **14**, 478 (2015)

Phase diagrams and CPW spectra
in GaV_4S_8 along the main three
cubic directions at 11K

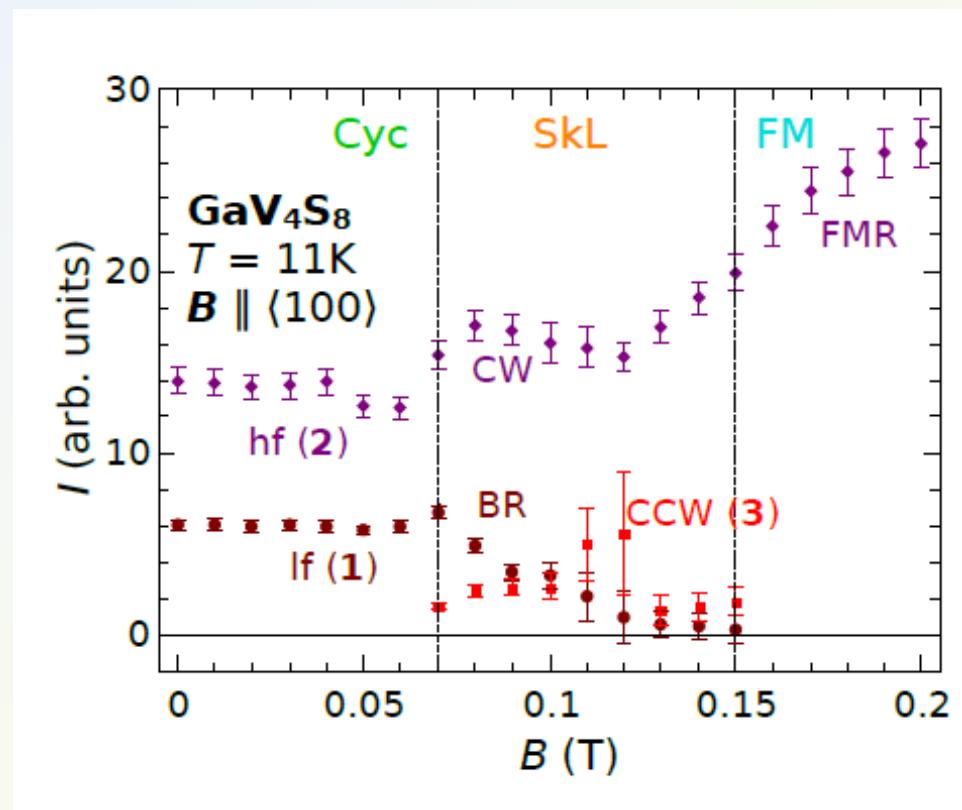
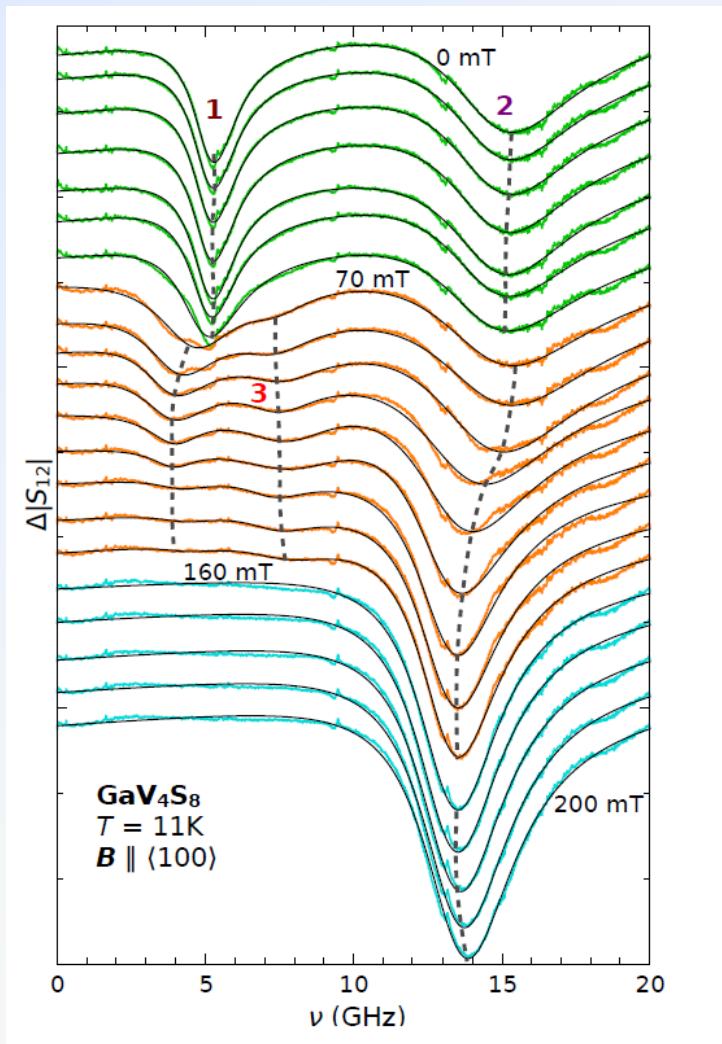
Shown are difference spectra, subtracting
the response at 2 T.

D. Ehlers et al., Phys. Rev. B **94**, 014406 (2016)



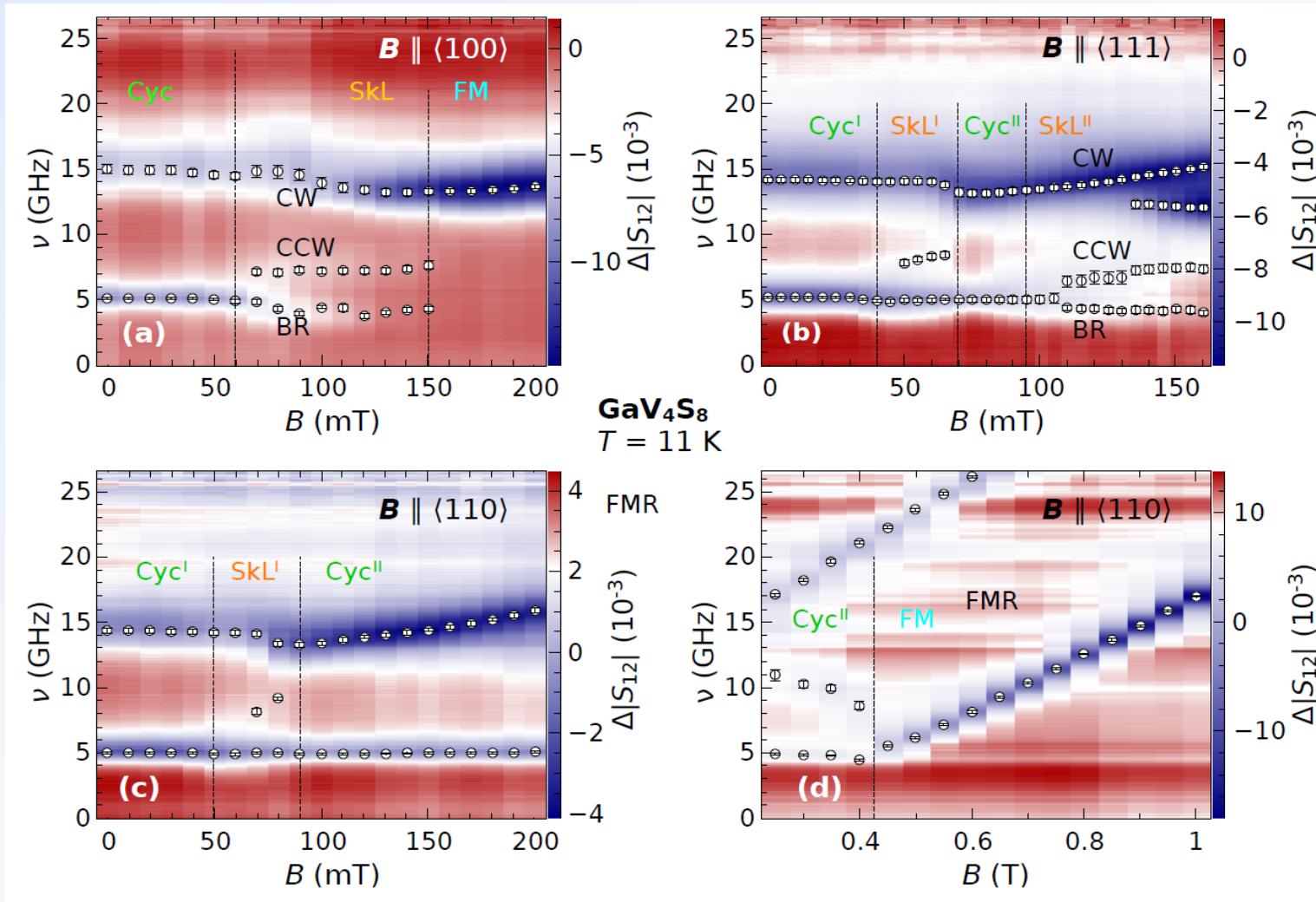
GaV_4S_8 : CPW absorption spectroscopy

CPW transmission spectra in GaV_4S_8 at a series of magnetic fields at 11 K. In the cycloidal phases breather (BR), counter-clockwise (CCW) and clockwise (CW) excitations appear.



GaV_4S_8 : CPW absorption spectroscopy

Color-coded plots of CPW transmission spectra in GaV_4S_8 in the frequency vs. magnetic field plane at 11 K. In the cycloidal phases breather (BR), counter-clockwise (CCW) and clockwise (CW) excitations appear.



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Skyrmions with ferroelectric polarization

- **Summary**
- **Lacunar spinels:** Interesting „new“ class of materials JT transition, orbitally-driven ferroelectricity. Complex magnetic and ferroelectric H,T-phase diagrams
- **Skyrmions in easy axis and easy plane magnets**
- **Multiferroicity:** Skyrmions dressed with FE polarization, spin-driven ferroelectricity via exchange striction
- **Magnetic excitations in collinear, helical and skyrmion phases:** In the SkL phase the sequence BR, CCW and CW mode is observed

Many thanks to
Experimental Physics V
EKM, University of Augsburg

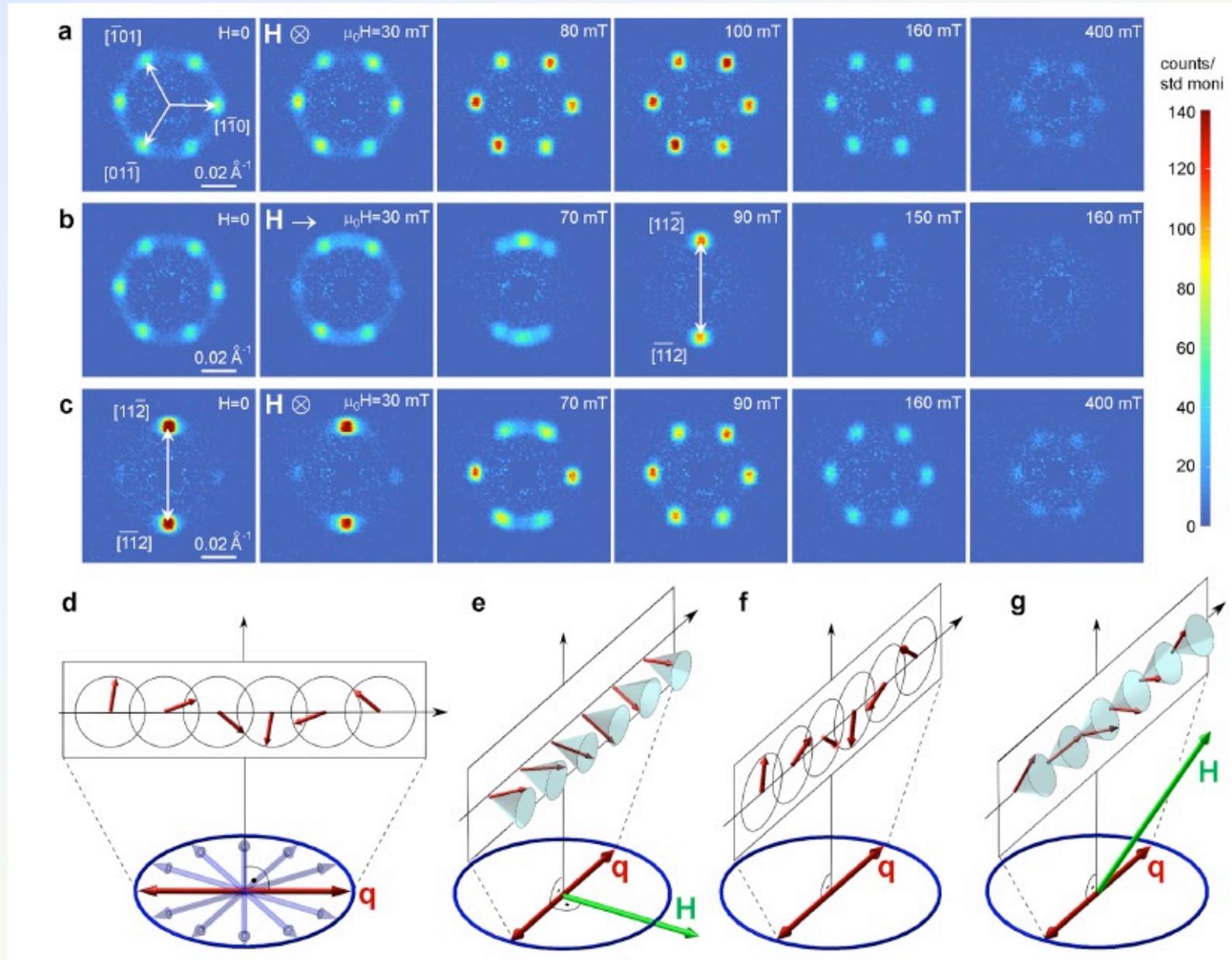


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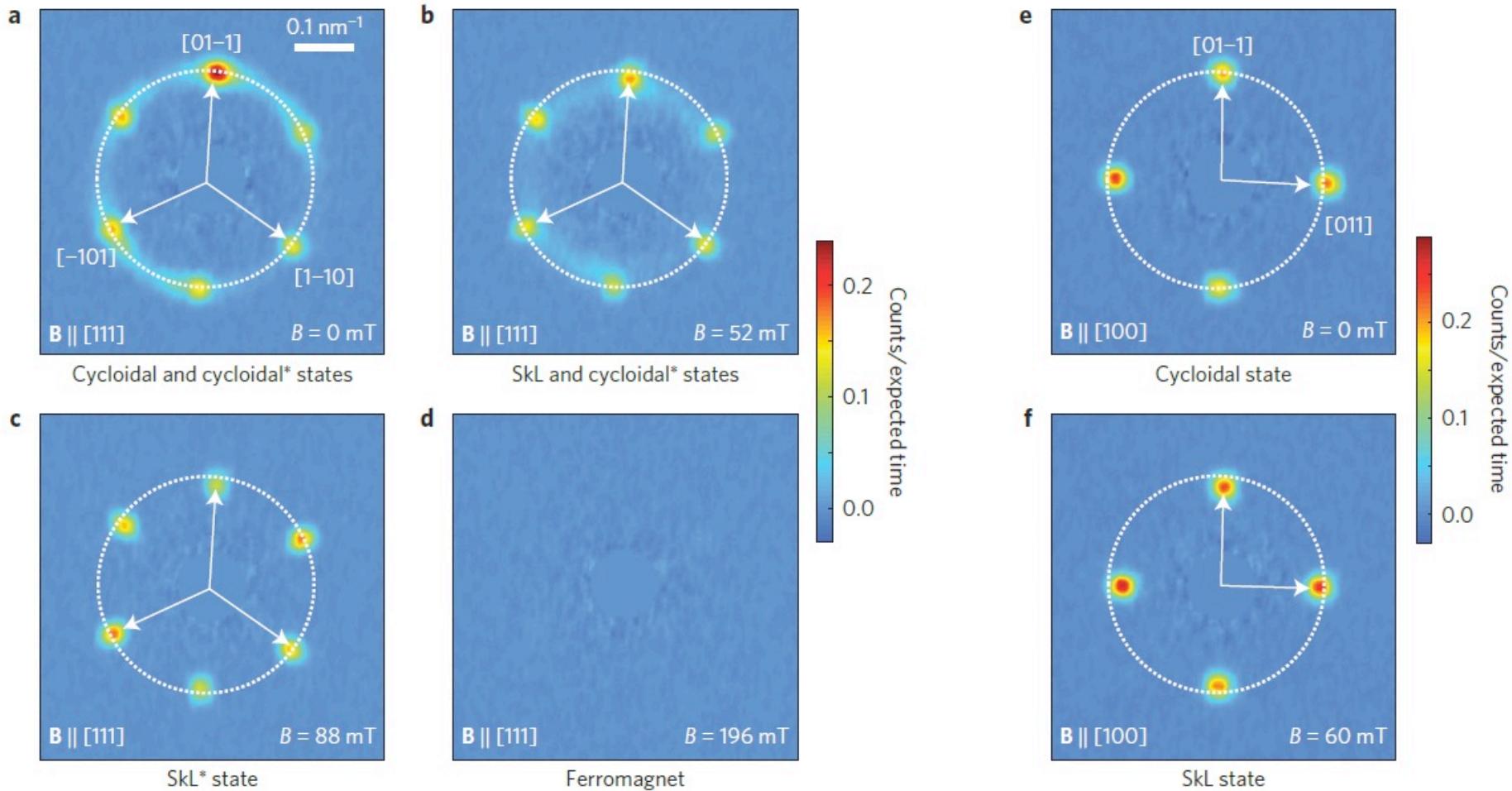


GaV₄Se₈: Neutron scattering

S. Bordács *et al.*, Sci. Reports 7, 7584 (2017)



GaV₄S₈: Neutron scattering



GaV₄S₈: CPW absorption spectroscopy

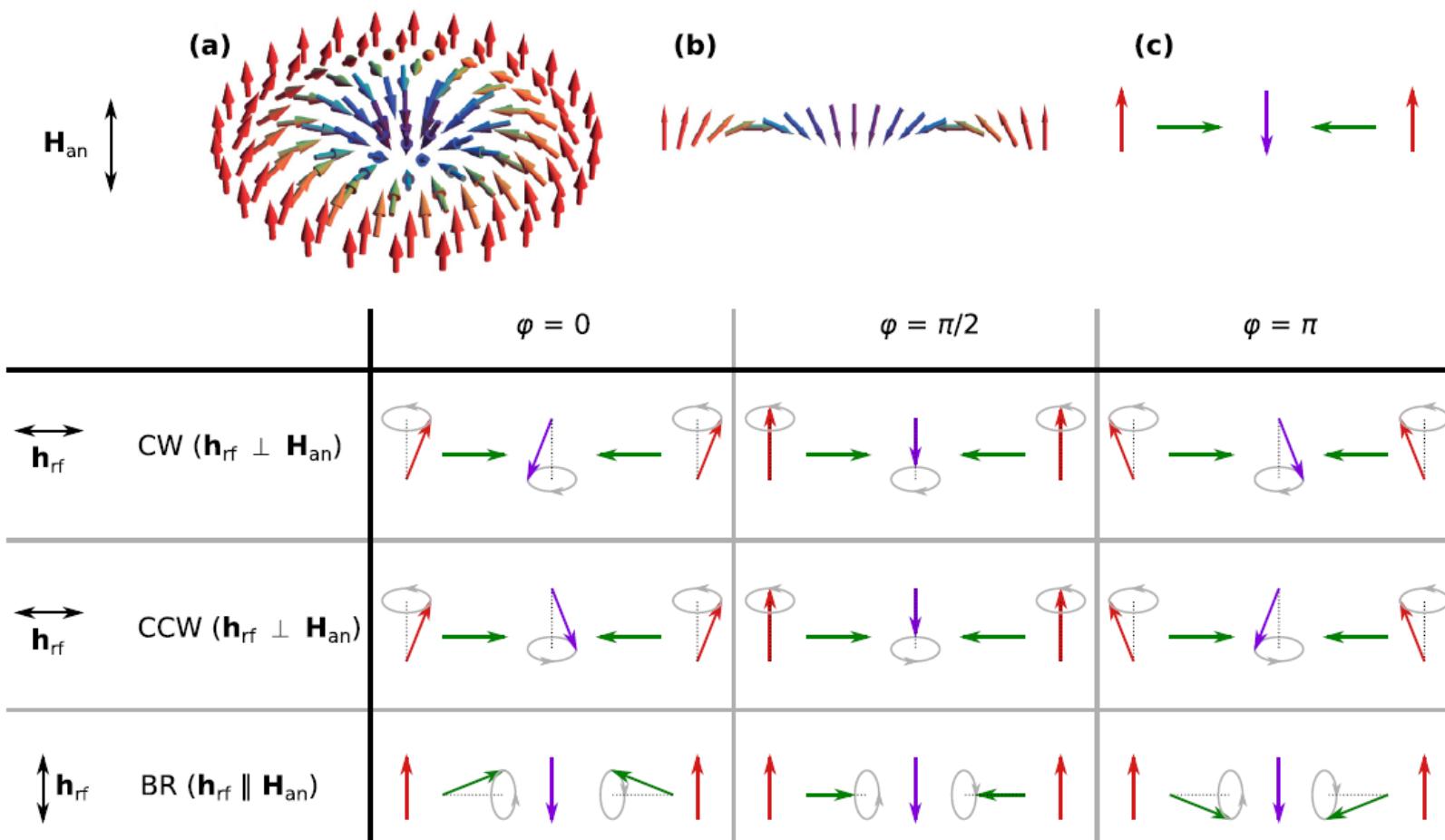
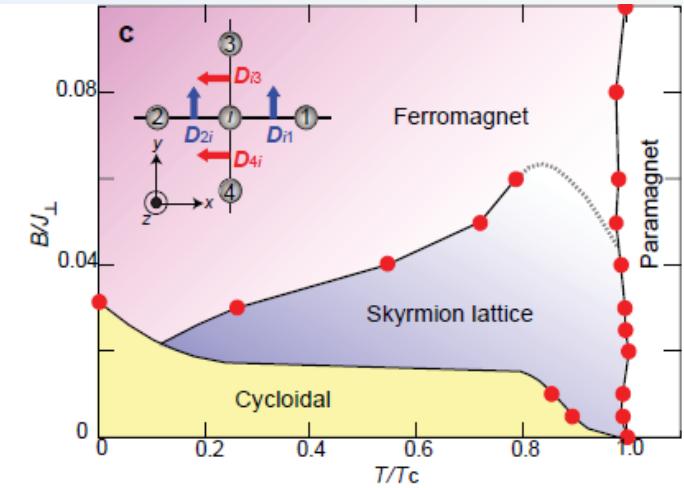


FIG. 5. Upper part: (a) Schematic illustration of a Néel-type skyrmion for a given easy axis of anisotropy \mathbf{H}_{an} . Each cross section (b) containing the skyrmion core corresponds to a spin cycloid and its simplification (c) to five spins comprises only vertical and horizontal arrows. Lower part: Table representing the spin dynamics of the five selected spins. The three rows stand for the three dynamic spin precessional modes (see text), whereas the three columns stand for three snapshots in time with corresponding phase φ . See the text for an explanation of the motion of the skyrmion core. The relation between the oscillating field \mathbf{h}_{rf} and the anisotropy field \mathbf{H}_{an} is different for CW and CCW modes as compared to the BR mode.

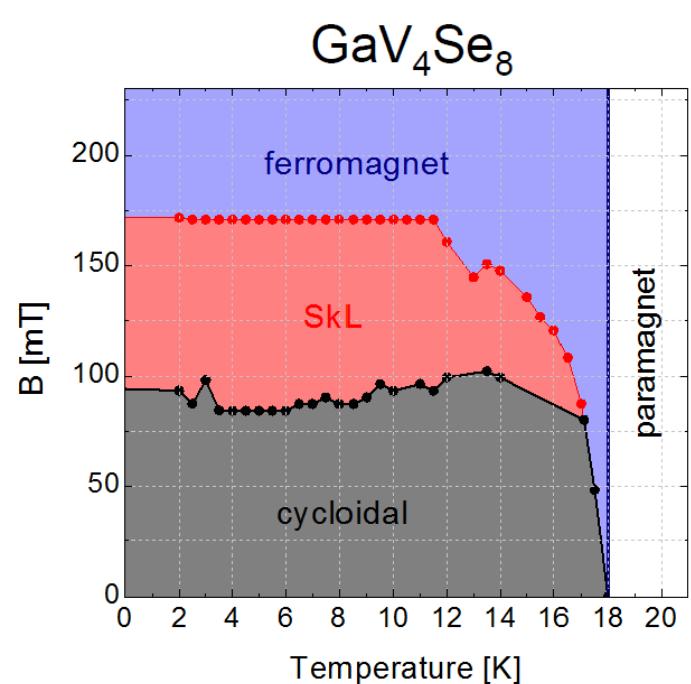
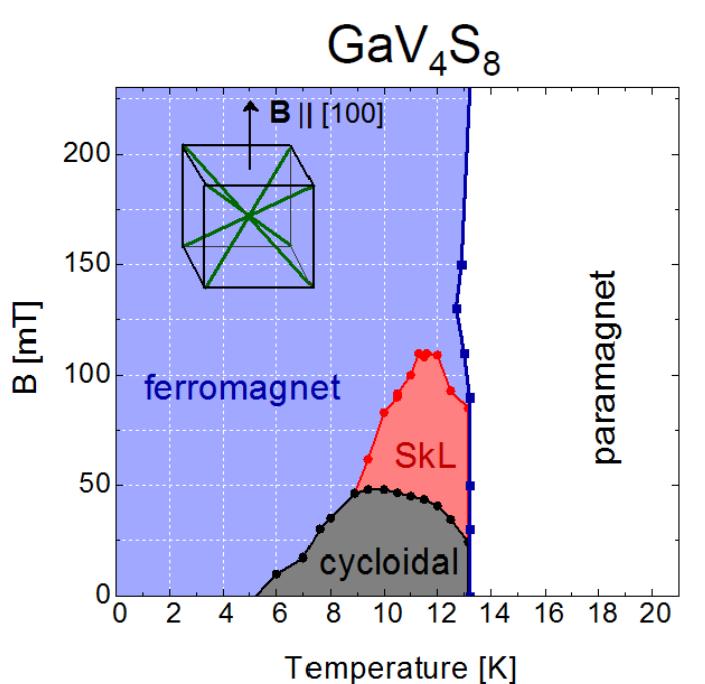
Lacunar spinels: Phase diagrams

Easy axis anisotropy favors ferromagnetism

Extended skyrmion phases under easy plane anisotropy



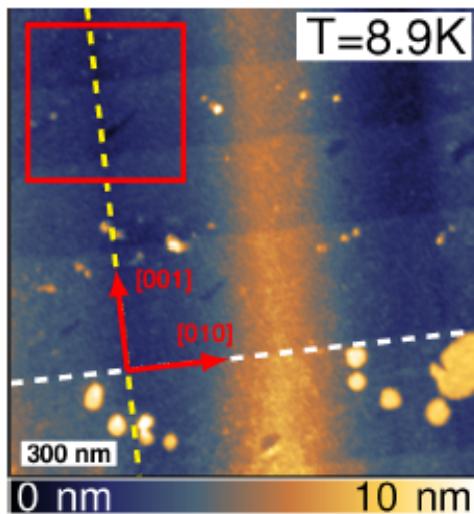
I. Kézsmárki *et al.*, Nature Mater. **14**, 1116 (2015)



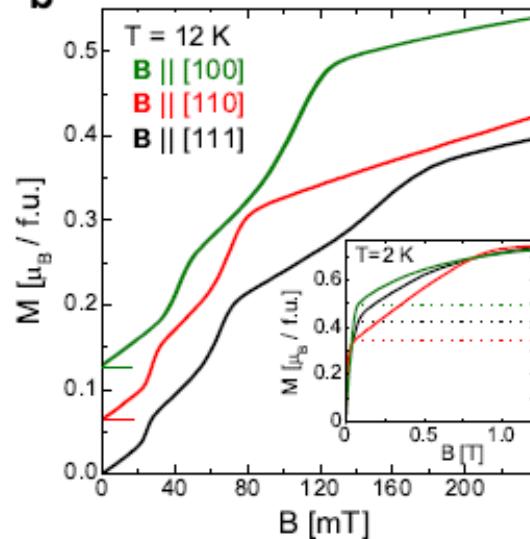
V. Tsurkan *et al.*, unpublished, 2016

GaV₄S₈: Skyrmion lattice

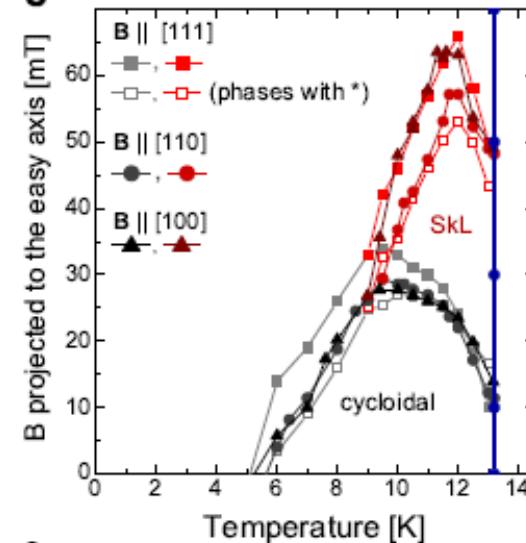
a



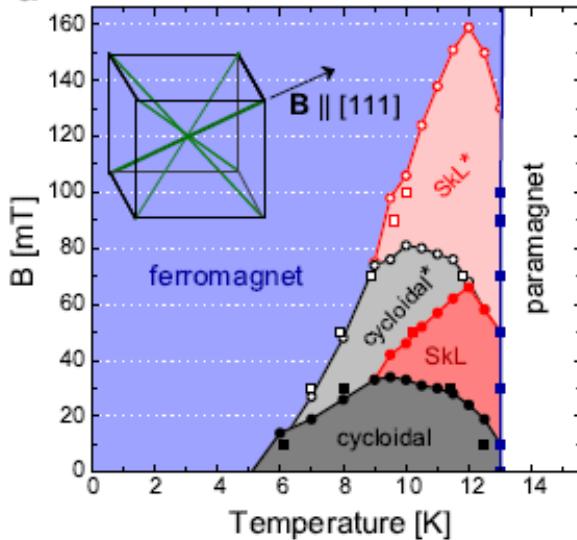
b



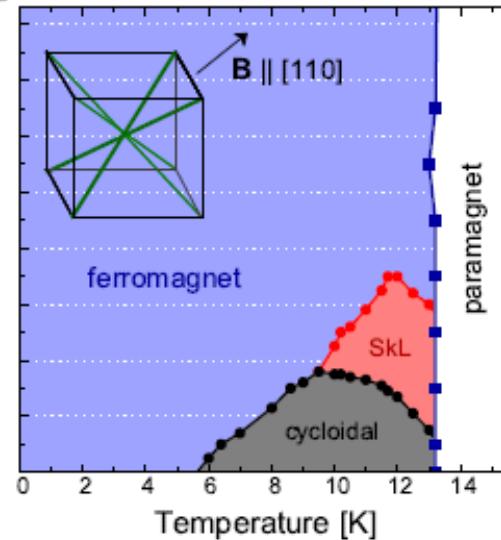
c



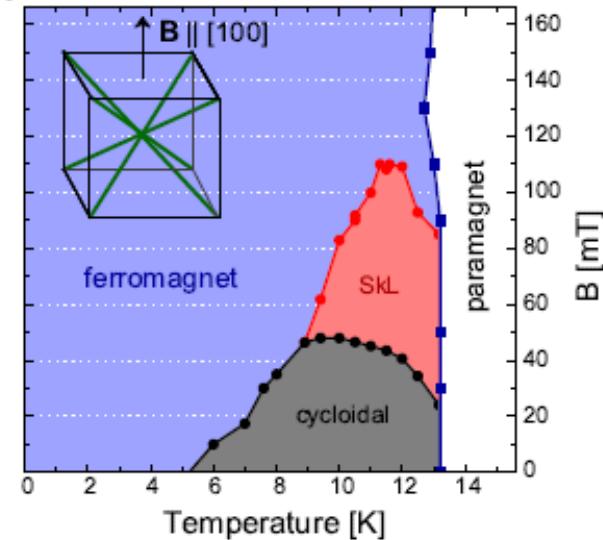
d



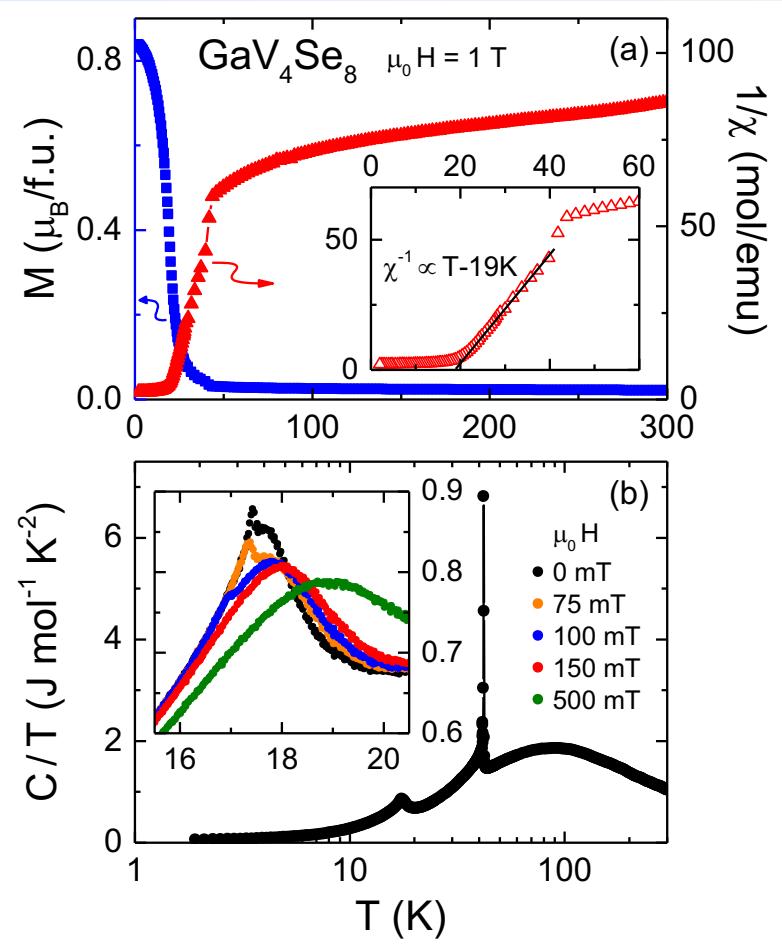
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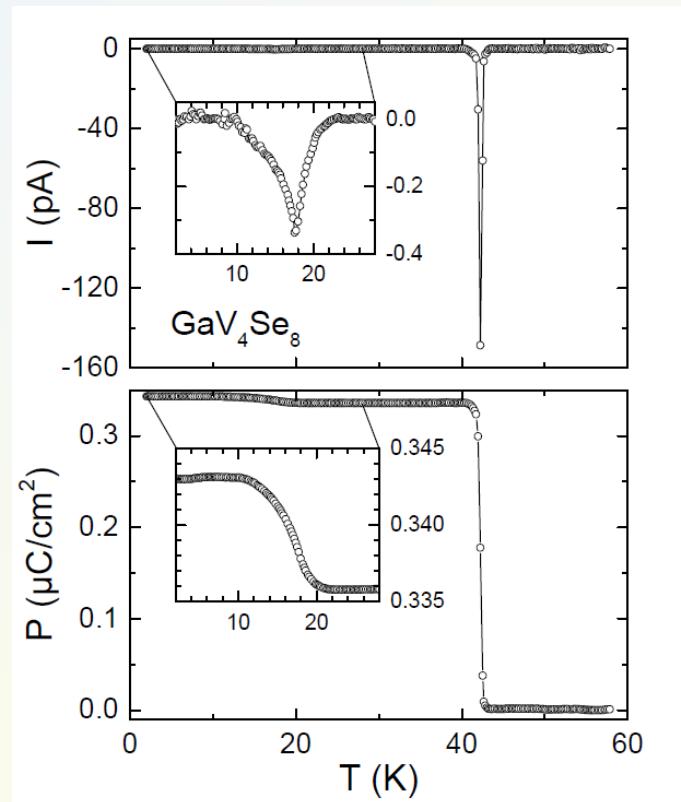


GaV_4Se_8 : Sample characterization



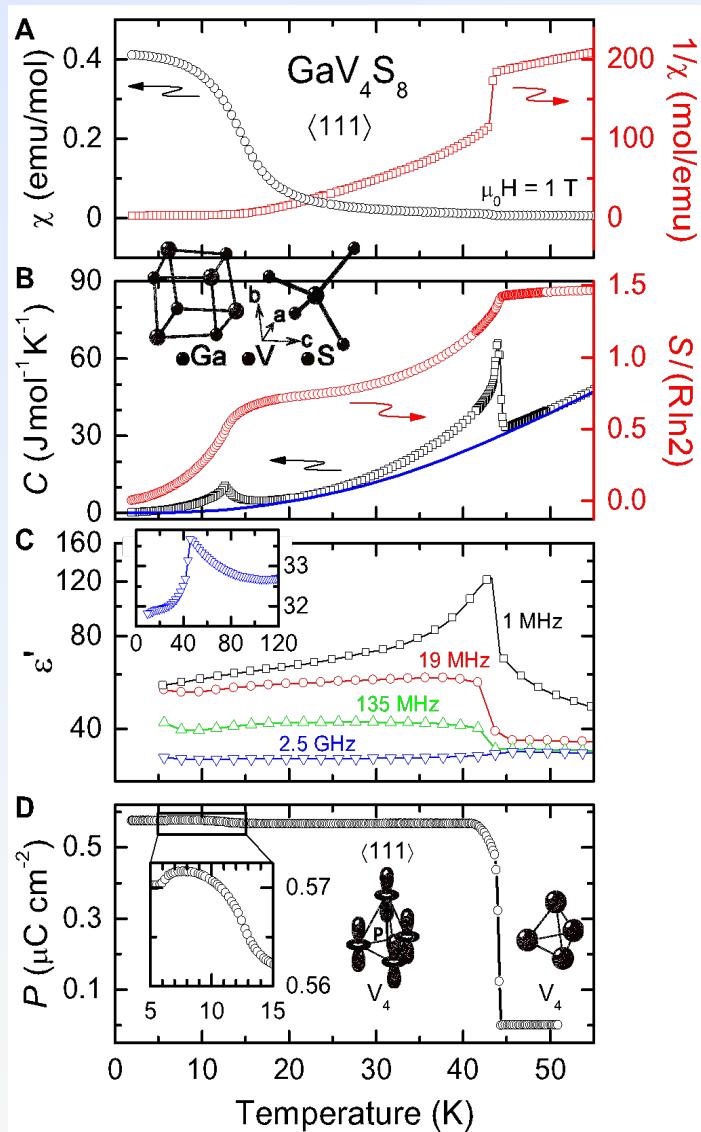
S. Widmann et al., unpublished (2017)

Jahn-Teller transition at $T_{\text{JT}} = 42\text{ K}$
induces ferroelectricity
Complex magnetic order below $T_c = 17.5\text{ K}$

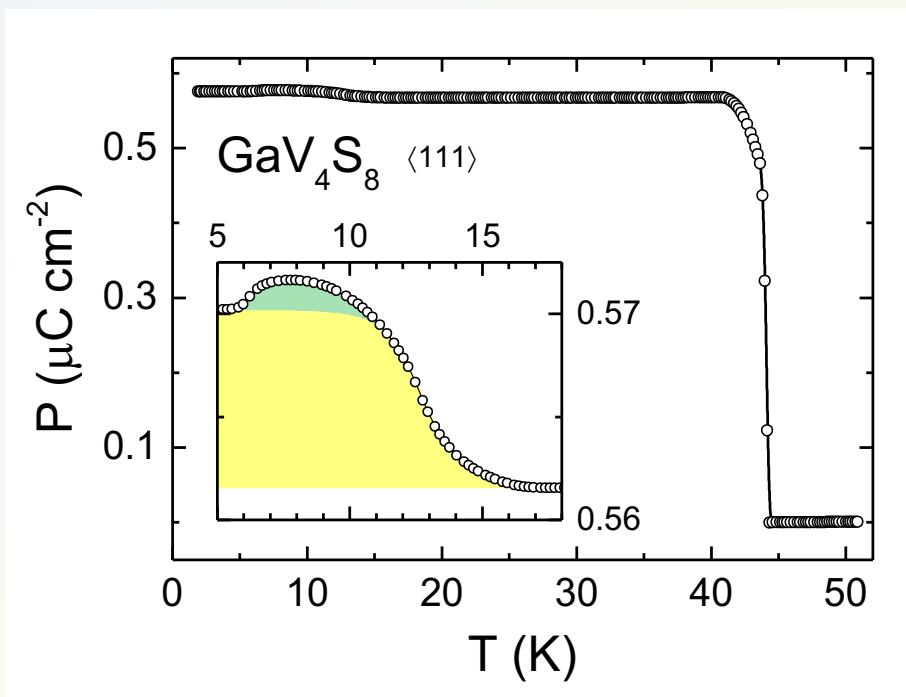


E. Ruff et al., unpublished (2017)

GaV_4S_8 : Sample characterization



Jahn-Teller transition at $T_{\text{JT}} = 44 \text{ K}$
induces ferroelectricity
Complex magnetic order below $T_c = 12.7 \text{ K}$

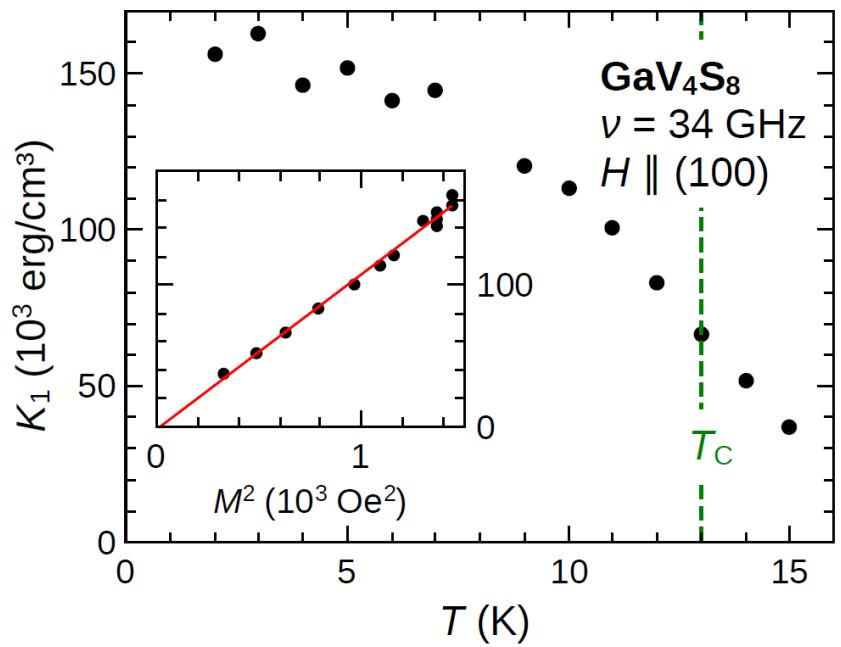


S. Widmann et al., Phil. Magazine (2016)
DOI: 10.1080/14786435

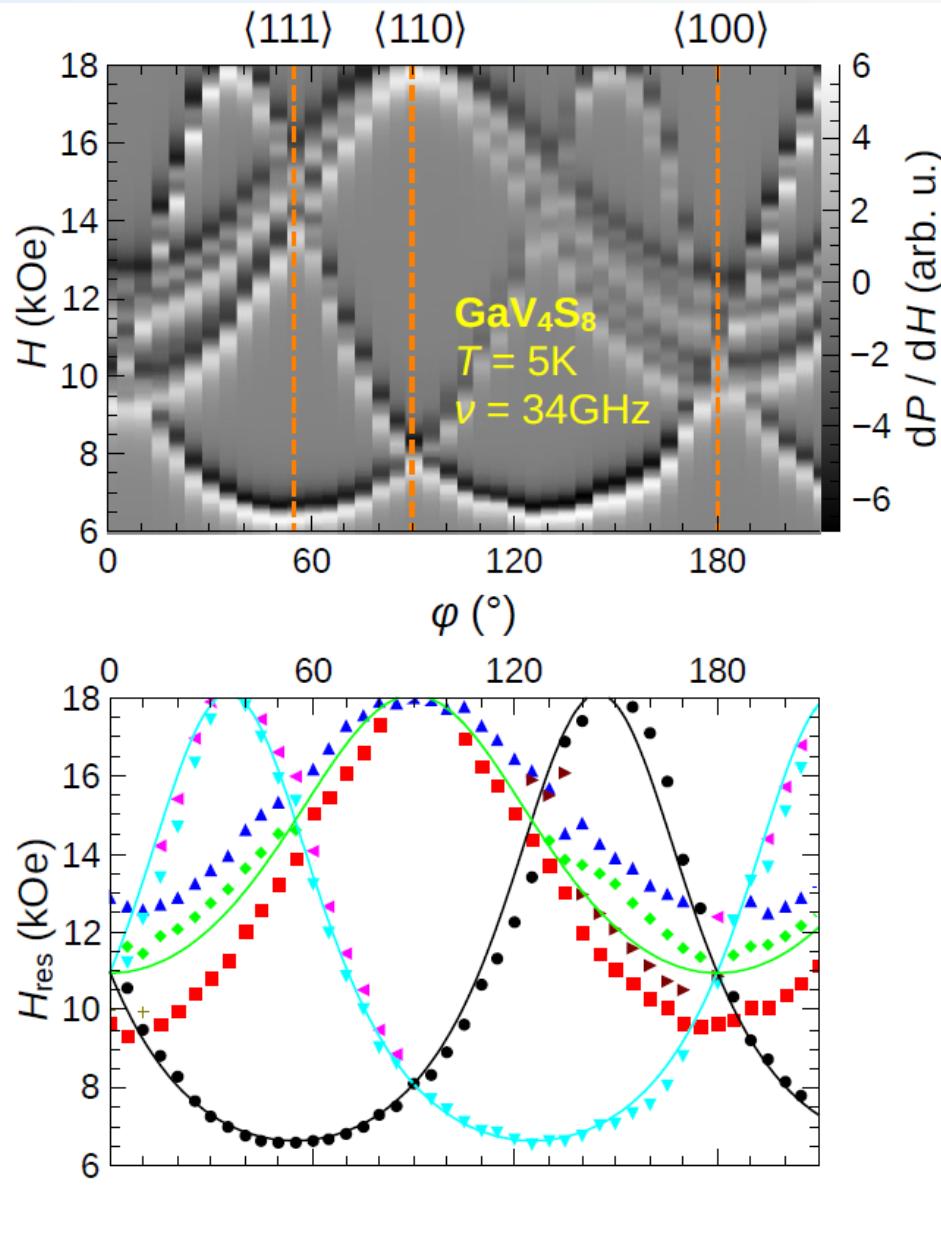
GaV_4S_8 : Q-band ESR

Magnetic resonance FM state:
Easy-axis Ferromagnet

- uniaxial anisotropy along $<111>$
- domain structure confirmed
- $K_1 = 7300 \text{ J/m}^3 \leftrightarrow z(J// - J\perp) \approx 1T$



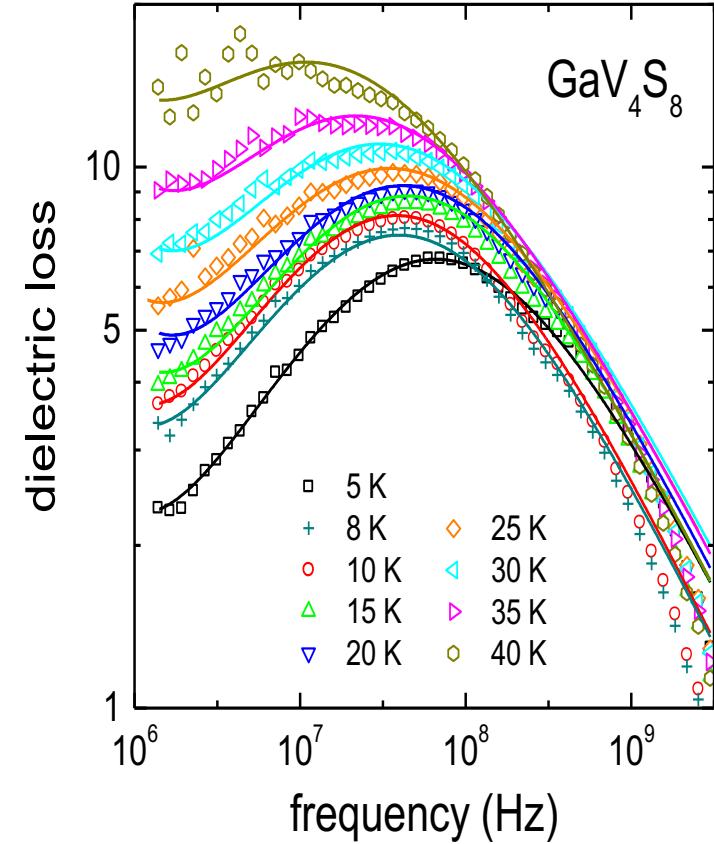
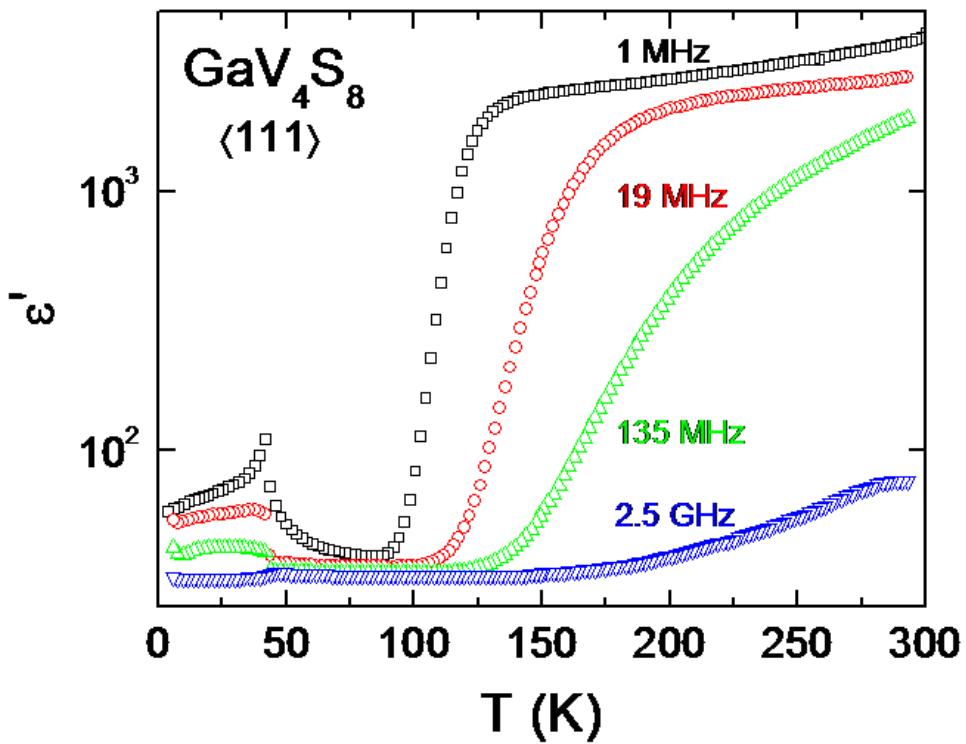
D. Ehlers et al., unpublished, 2016



Angular dependence of
resonance field in GaV_4S_8 in (110) plane

GaV_4S_8 : Dielectric spectroscopy

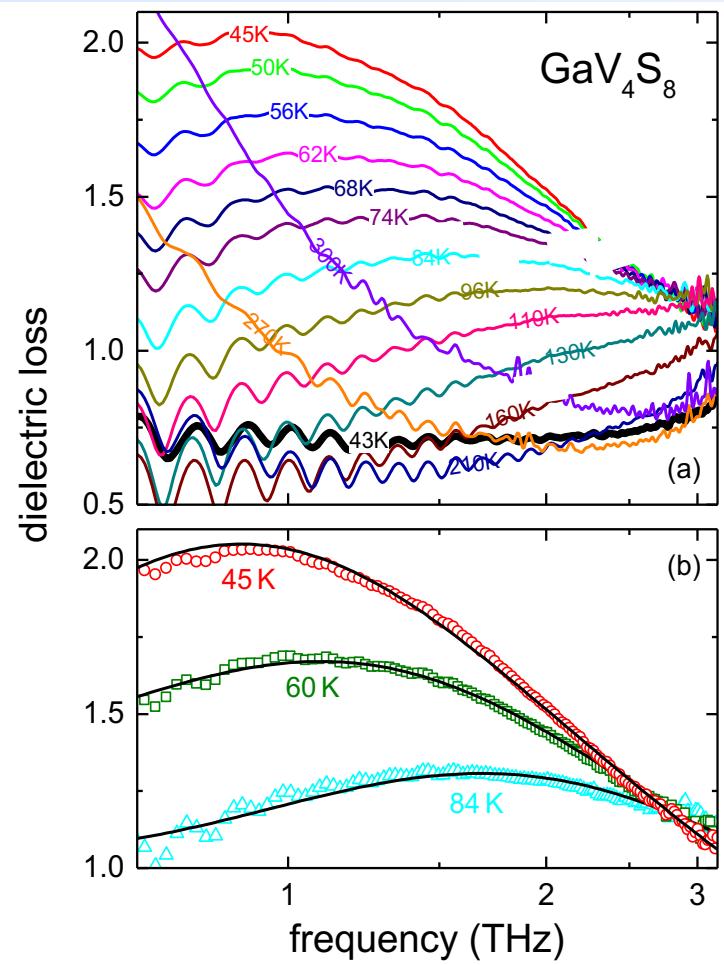
High-frequency dielectric spectroscopy at Jahn-Teller transition:
Fingerprint of orbital fluctuations?



$$T < T_{JT}$$

Slowing down of relaxational mode
approaching the phase transition
on increasing temperature

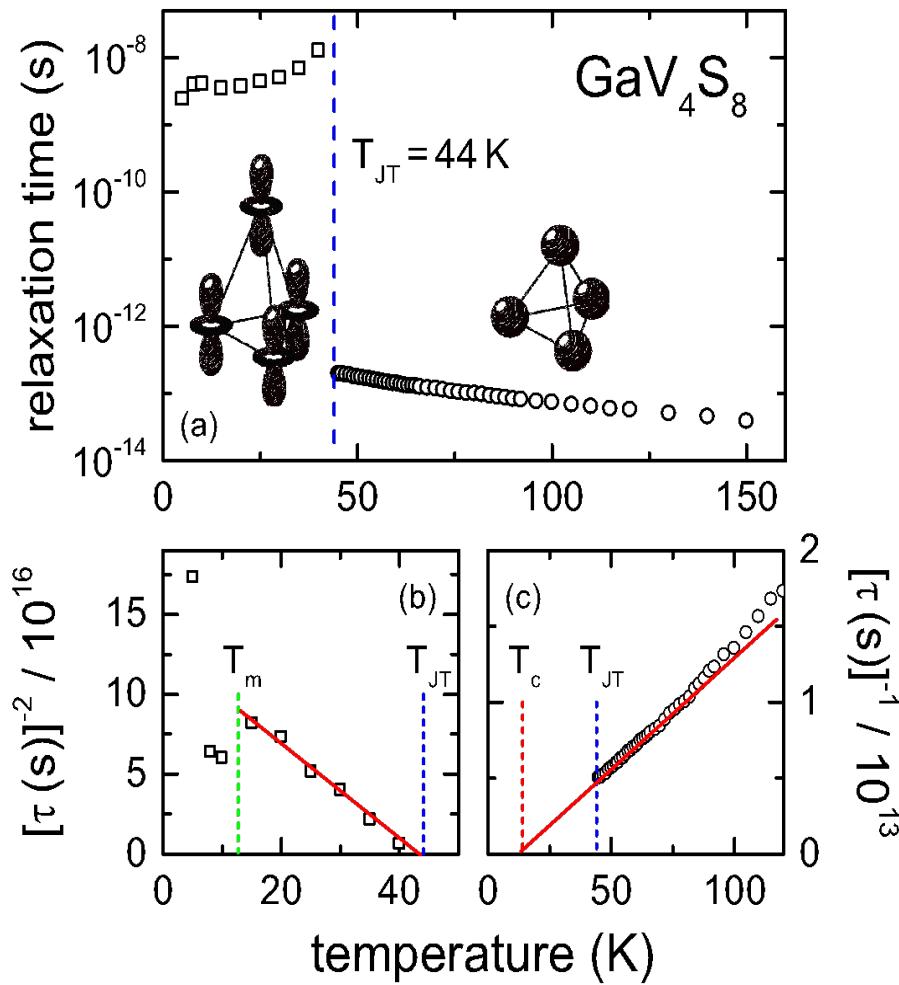
GaV_4S_8 : THz spectroscopy



Slowing down of relaxational mode
on decreasing temperature

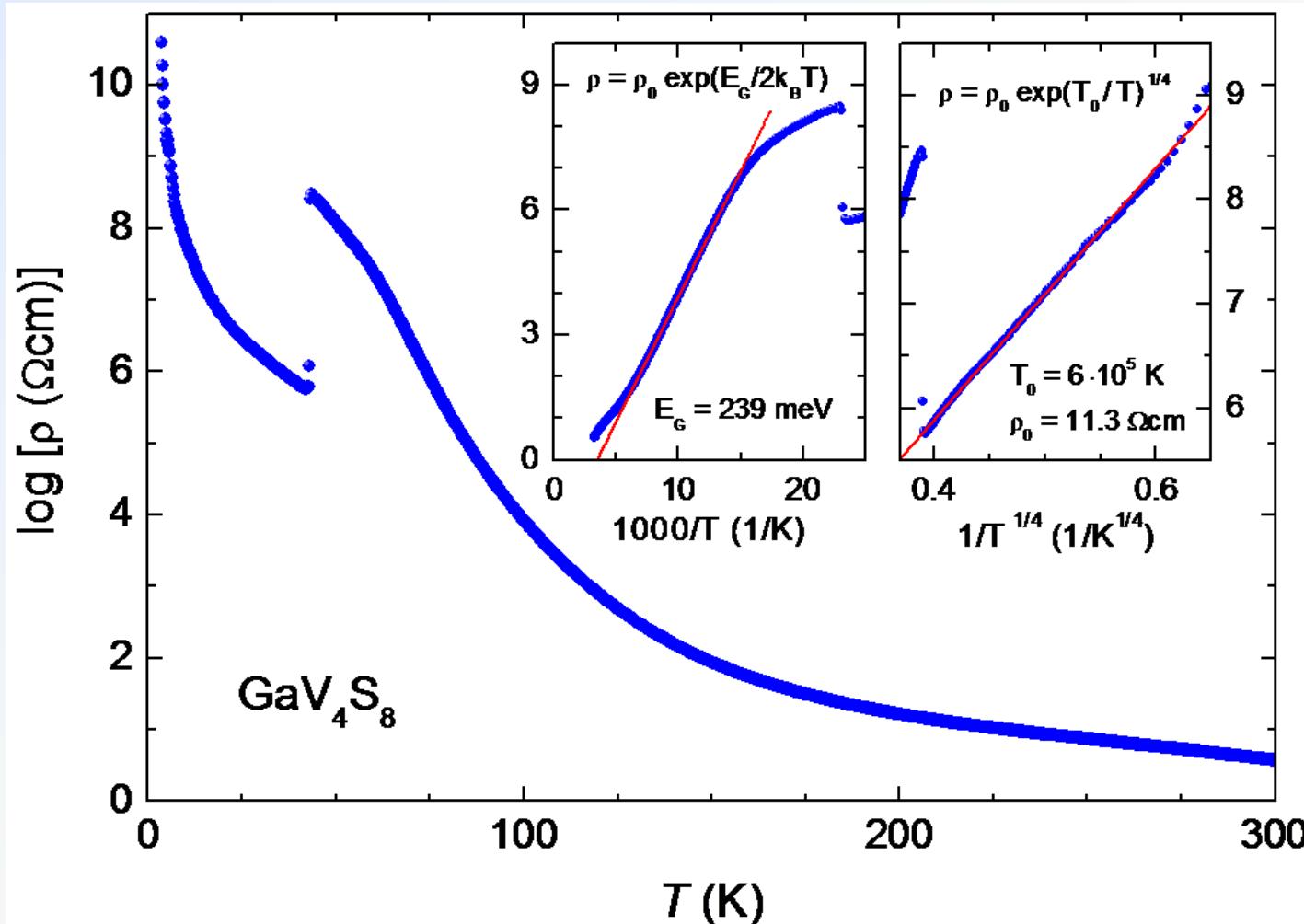
$$10 \text{ cm}^{-1} = 1.24 \text{ meV} = 300 \text{ GHz} = 14.4 \text{ K}$$

Orbital order driven ferroelectricity



GaV₄S₈: Sample characterization

Resistivity: Three orders of magnitude reduction at Jahn-Teller transition T_{JT} = 44 K
Thermally activated behavior for T > 44 K with band gap E_g = 239 meV
Hopping conductivity (VRH) for T < 44 K



GaV_4S_8 : Sample characterization

Specific heat: Contributions from phonons and magnons

Well defined anomalies at $T_{\text{JT}} = 44 \text{ K}$ and $T_C = 12.6 \text{ K}$

Small anomaly at $T_m = 5 \text{ K}$ (cycloidal to FM transition)

No field dependence of T_{JT} ; strong field dependence of T_C

